An Investigation into Nanoparticle Fabrication

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Abstract

In this paper, methods of fabricating gold nanoparticles are investigated with respect to their feasibility within the context of the Bethel University Nanotechnology Lab. Of the two methods investigated, electrodeposition by field-induced atomic emission was not accomplished, but thermal deposition onto exposed PMMA resist proved to have high potential for successful nanoparticle fabrication.

Introduction

Nanoparticles are of importance in many fields, such as material science, electrical engineering, optics, and, of course, nanotechnology. Particularly, gold nanoparticles have applications in optical/plasmonic tweezing, solar cell doping, cancer treatment, infrared detectors, and many other uses. However, a challenge facing many scientists and engineers is developing a method to fabricate such particles. One such method, which is explored in this paper, is electrodeposition by electric field-induced atomic emission. Essentially this method involves applying a voltage across a gold wire and silicon chip, separated by a sub-nm gap. This creates an electric field, and some gold atoms migrate from the tip of the wire to the silicon chip. Now, in order to accomplish this, one must have a means to control the tip of the wire in three dimensions, as well as keep it very close to the surface of the chip. A tool that works well for this purpose is an Atomic Force Microscope (AFM). Knowledge of the basic principles of the mechanisms and operation of the AFM are necessary if one is to follow this procedure.

Atomic Force Microscopy (AFM)

Operation of an AFM relies on the dipole-dipole interaction between atoms. An AFM utilizes these forces to map out a topographic image of a surface. A small quartz tuning fork, shown in Figure 1, is attached to the AFM, and when a voltage is applied to the tuning fork, it resonates at its specific resonance frequency. A very sharp tungsten tip, ideally with an apex diameter on the order of tens of nm or less, is attached to the end of the tuning fork. A photograph of one such is shown in Figure 1. When the sharp end of this tip comes very close to the surface being imaged (gap one nm or less), the dipole-dipole interaction from the atoms in the tip and the atoms in the surface damp the resonance of the tuning fork. The AFM system moves the tip up or down to to hold the damping constant as the tip is moved across the surface, and a topographic image of the surface can be

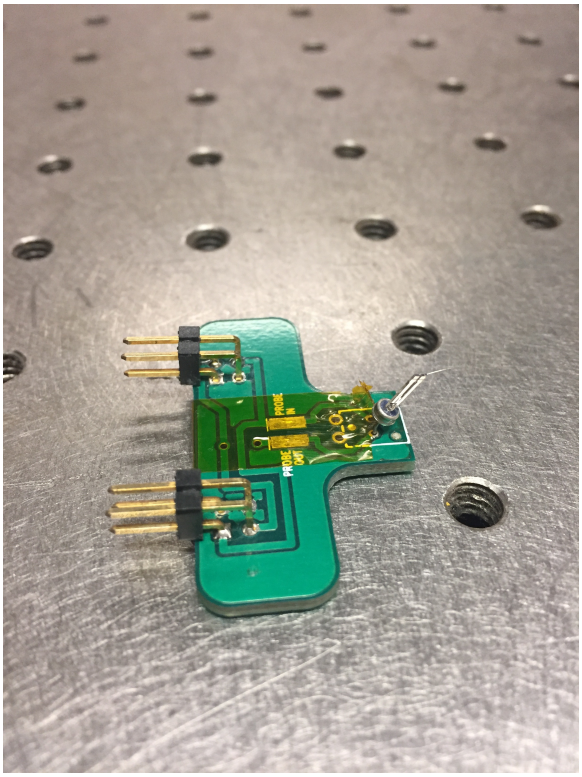

Figure 1: Tuning fork probe

generated. To use an AFM for electrodeposition, the tungsten tip is replaced with a gold wire, which is then connected to the negative terminal of a function generator. A silicon chip is used as the deposition surface, with a small piece of indium melted onto a corner as an electrical contact, which is in turn connected to the positive terminal of the aforementioned function generator. For the purposes of this lab, a *GWInstek AFT-2125* was used. However, there are many hurdles to overcome in making this process work effectively, as the author of this paper discovered. For the AFM to function properly, the tuning fork must be electrically isolated. This proved to be somewhat difficult, as the gold wire (which has a voltage applied to it) is glued to the tuning fork, causing the electrical pulses applied to the tip to interfere with the AFM resonance feedback loop. However, it seemed that this interference could be overcome, and the experiment was able to continue. An image of one of these tips with a gold wire glued to a tuning fork is shown if Figure 2.

Tip Preparation

An important aspect of this process is the sharpness of the tip used for imaging/deposition. The tungsten tips for conventional imaging were prepared using electrochemical etching in a KOH solution. The wire to be used for the tip is placed

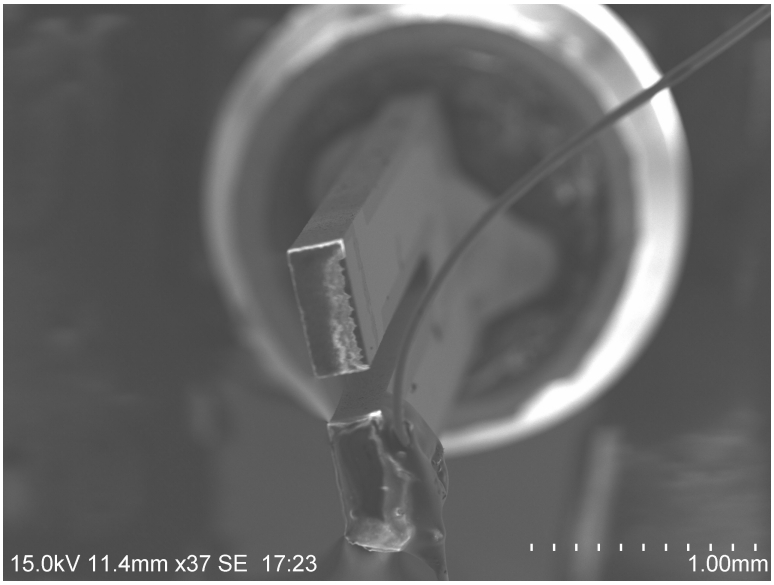

Figure 2: Tip made with gold wire

through a small copper ring, which acts as the anode, and into the KOH solution. A meniscus of KOH solution is formed on the copper ring around the wire, and a voltage is applied between the copper ring and a separate wire placed in the solution. Current flows and the tip is etched until the weight of the lower portion of the wire causes the wire to break, and the connection is broken, stopping the etching process. This method works well for AFM because it produces a very sharp tip, and the sharper the tip, the more accurate the image it produces. However, the tip used for deposition must be gold, which cannot be etched in the KOH solution. As such, an alternative method must be developed. The initial method proposed was to use a very sharp wire cutter to snip the gold using a "pulling" motion as the wire is cut. The hope here is that the wire will be stretched as it is cut, providing a sharper tip than just chopping the end of the wire with no tapering. Some of these tips were imaged using a Scanning Electron Microscope (SEM), and these are shown in Figure 3.

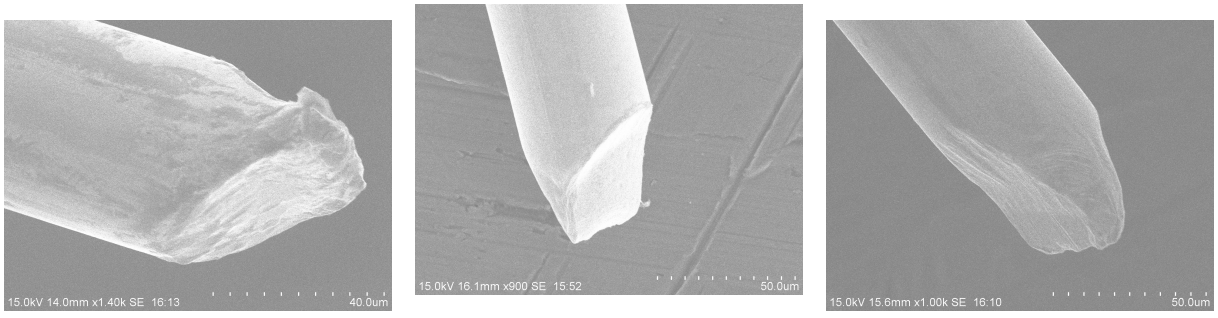

Figure 3: Cut gold tips

Imaging

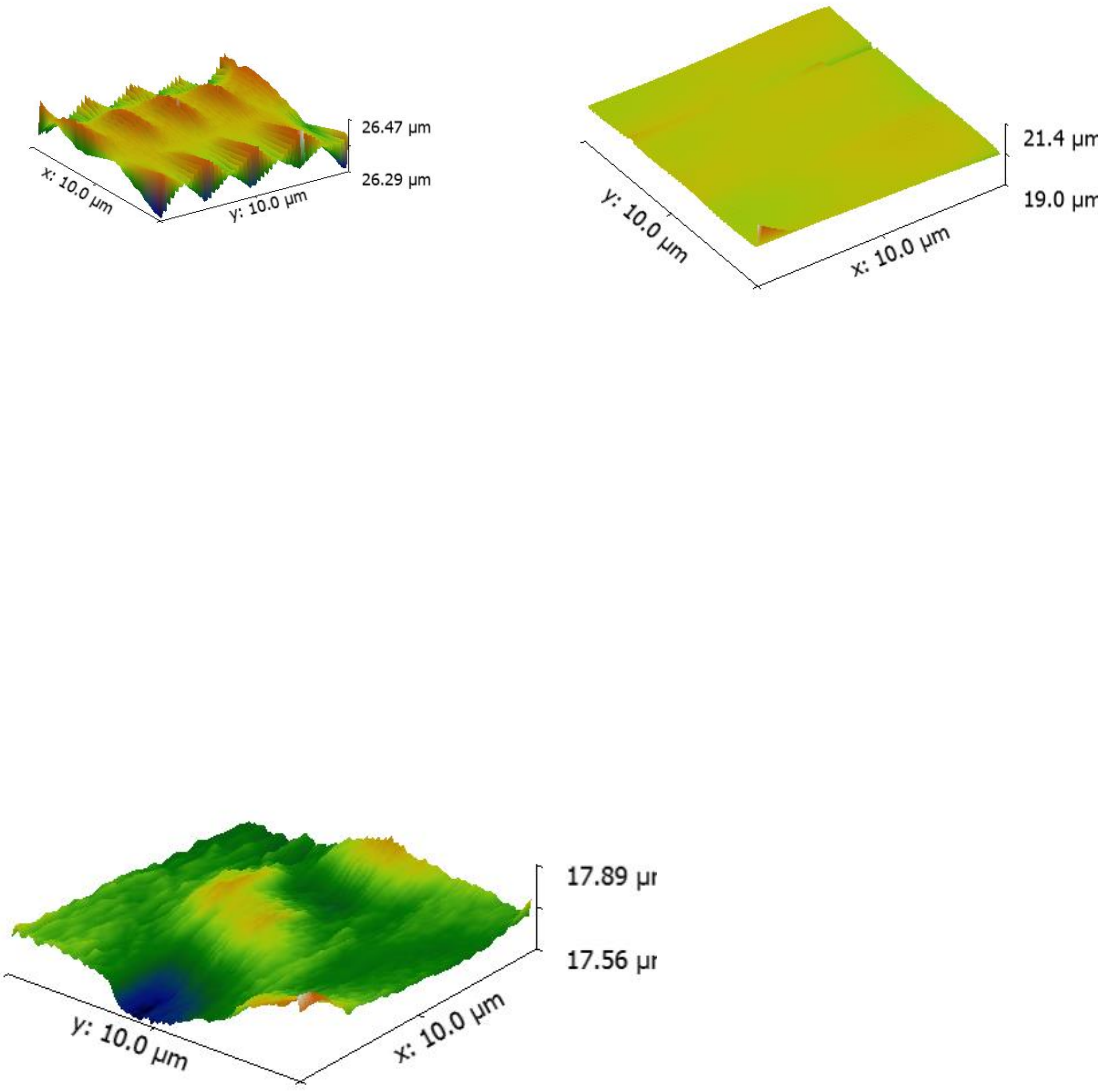

Figure 4: AFM scans with gold tip

Once tips were constructed, the next step was determining their effectiveness/accuracy in imaging a surface. Several scans were taken using these tips, some of which are shown in Figure . The primary goal of these scans was to determine if the gold tips would accurately image the topography of the surface (i.e. flat, curved, rough, etc), if the images were reproducible (if two scans of the same surface generated the same image), and the resolution of the images (minimum size of surface features that can be imaged).

In taking these scans, it was found that these tips often exhibited unpredictable behavior. There were many instances were an image would not accurately depict the surface, or two scans of the same surface would appear different. However, once the system was recalibrated a few times, the tips seemed to function better, and more accurate images were taken. It was found that the images were accurate to about 1 μm, indicating that the tips had an apex diameter on the order of a few μm.

Deposition

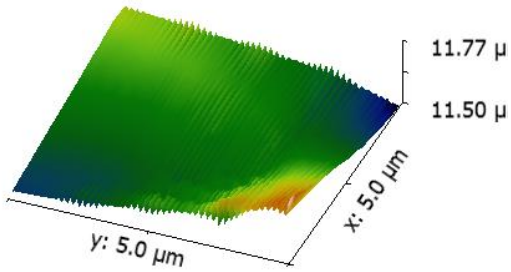

Figure 5: Before attempted deposition

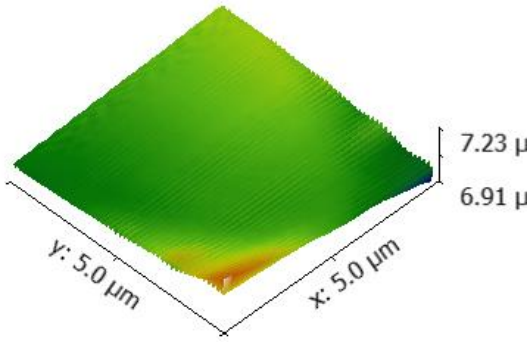

Figure 6: After attempted deposition

In developing a method for electrodeposition, the voltage applied to the tip must be pulsed (rather than continuous, i.e. DC), as this is meant to create small nanoparticles with each pulse, rather than a continuous deposition. The pulses should alternate between zero and a positive voltage, so signal from the function genera-

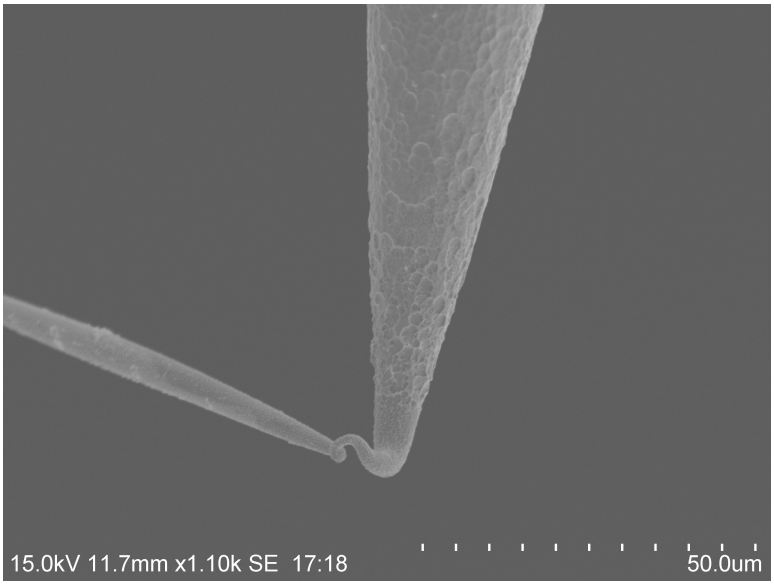

Figure 7: Etched gold tip

tor must have a DC offset to always stay above zero. The primary variable then, is the strength and duration of the pulses. In [1], it was recommended to use a tip-negative voltage of 20 V, with pulses from 0.2 - 200 milliseconds. Clearly, this is a rather broad range, so some experimentation was needed. The end of the gold wire used for the tip was connected to the negative terminal of the function generator, and an alligator clip connected to the positive terminal was clamped on the indium contact of the silicon wafer. The method for testing deposition is as follows: first, with no voltage applied, a scan is taken of a square area with edges 5-10 μm in length. Then, another scan is performed, this time with the voltage pulse applied, over a 1 μm^2 area in the middle of the initial area. Once that is finished, the voltage is turned off, and another scan is taken of the first, larger area. By comparing the first and last scans, the hope is that the deposited nanoparticles can be observed. At first, 20 V seemed rather high, so the initial bias was 1 V, and was increased from there. Since the recommended pulse duration covered such a wide range, an initial pulse of 1 ms was chosen, corresponding to an output frequency of 1 kHz from the function generator. Images of the before and after scans from this trial are shown in Figures 5 and 6. These scans show essentially the same surface topography, indicating a lack of deposited gold nanoparticles. In subsequent tests, the voltage was increased to 2, 5, 7.5, 10, and 13.6 (the maximum output amplitude of the function generator) V, and pulse lengths were varied to 2, 4, 10, 50, and 100 ms. Despite these variations, no gold deposition was observed. It was suggested that perhaps scans were being taken too quickly, and the probe tip was not picking up the small surface imperfections indicating gold deposition. To test this hypothesis, several scans were taken at slower speeds. This slowed-down process was accomplished by extending the read/write delay in the scanning feedback loop. The standard delay is 10 ms, so scans were taken with delays of 20, 40, and

even up to 100 ms, but these scans still did not indicate the presence of nanoparticles. After some frustration and review of the literature, it was noted that many other papers used tips much sharper than the 1 μm tip used here. The decision was made to try electrochemically etching gold tips, similar to the Tungsten tips etched previously. In reference [3], gold tips were etched using a solution 0.5 M in HCl and 0.5 M in H_2SO_4. This solution was prepared, and etching was accomplished using an applied voltage of 24 V DC in about 10 minutes. Etching appeared successful, so deposition was tried using this tip, but nanoparticles were not observed. Seeking insight into why deposition was again a failure, the etched tip was imaged in the SEM, and this image is seen in Figure 7. As can be seen, the tip does not have the nanometer sharpness that is desirable, but instead exhibits a curl at the end. This is most likely due to the softness of gold compared to Tungsten. In the etching process, instead of making a clean break at the tip as Tungsten does, the gold may have stretched and broke instead, causing the tip to recoil and form the curl shape seen in the figure. This tip geometry explains why it failed to deposit any nanoparticles.

PMMA Resist Exposure

At this point, upon further review of the literature, it was noted that nanoparticles fabricated in Reference [2] were only a few hundred Angstroms in height and diameter. While the AFM is capable of taking images at this vertical resolution, there is often noise on this scale, so it is possible the AFM may not have imaged the nanoparticles. However, it is much more likely that the poor tip geometry was interfering with successful deposition. As such, the research advisor proposed an alternative method to fabricate gold nanoparticles by etching PMMA and then using a thermal deposition chamber. The method for such a procedure is outlined as follows.

PMMA, or Poly(methyl methacrylate), is spin-coated onto a silicon chip, which produces a coating on the chip a few hundred nm thick (here, 950 K molecular weight PMMA is used). Reference [4] advised using a PMMA coating around 20 nm thick, so the coating used in this process is not ideal, but due to time constraints of this project, it was used anyway. The coated chip is then placed on the imaging stage of the AFM and connected to the positive terminal of a DC power supply. The negative terminal connected to the AFM wire tip. When the DC voltage is applied between the AFM tip and the PMMA-coated silicon chip, electrons tunnel from the AFM tip to the silicon, leaving behind an area of broken-up polymers where the PMMA was. The chip is then placed in a developer solution of 1 part MBIK to 3 parts isopropyl alcohol. The developer removes the broken-up polymers, exposing a small area of silicon which acts as a mold for gold to be deposited into. While Reference [4] used a tip-negative bias of 40 V DC, the method performed here used 63 V. This was done because the PMMA coating was much thicker than that used in [4], and 63 V is the maximum output of the DC power supply. When using the AFM tip to expose an area of PMMA, it

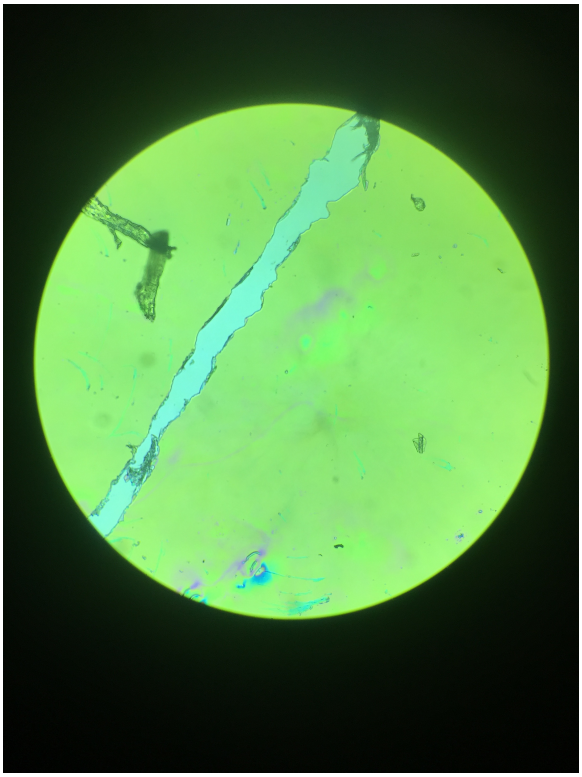

Figure 8: Microscopic image of removed PMMA

was decided to expose three square areas of 25 μm^2 each, arranged geometrically, in order to make the results more easily observable. After the chip was placed in the developer solution for about 30 seconds, it was examined initially under an optical microscope. This examination did not indicate successful removal of the PMMA substrate. The procedure was was tried a few more times, but to no avail. At this point, the researcher decided that perhaps something just wasn't working quite correctly in the AFM set up, and decided to try exposing the PMMA manually. To yield clearer results, a 0.25 mm diameter wire was used, rather than the 0.05 mm gold wire used previously. The wire was placed in a precision manipulator and connected to the negative terminal of the DC power supply and 63 V was applied. As before, the positive terminal was connected to the PMMA-coated silicon chip. The wire was contacted to the chip and maintained contact for about 15 seconds. The power supply indicated a current 0.01 A was flowing at this time. Contact was then broken, and the wire was touched to the chip in a few other places for about the same amount of time. The chip was then placed in the developer solution for about a minute and examined under an optical microscope.

This indicated large areas of exposed silicon where the wire contacted the chip. An image of one of these areas is shown in Figure 8. The elongated shape of this area indicates that the wire actually scraped across the surface as it made contact,

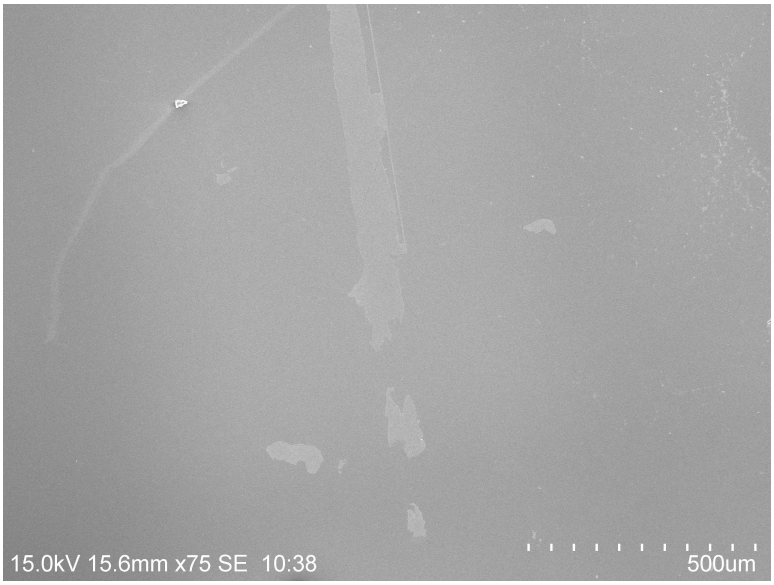

Figure 9: Areas showing chromium deposition

rather than just at single point. In any case, the PMMA was removed in this area, so the procedure was continued, and deposition was attempted. While the initial plan was to fabricate gold nanoparticles, at the time of the experiment the thermal deposition chamber was only set up to deposit chromium. Due to the time constraints of the project, chromium was used, the idea being that, if the process worked with chromium, it would work with gold. The deposition chamber was often extremely uncooperative during this process, but eventually 50 nm of chromium was deposited onto the chip. The chip was then placed in an acetone bath. This breaks down and removes PMMA coating, leaving behind only the chromium that was deposited directly onto the silicon, and not the PMMA. After resting in the acetone for a few minutes, the chip was examined under an optical microscope. This was rather unclear, as the etched areas appeared essentially the same as before deposition. The chip was then imaged in an SEM, as the SEM is more effective in conveying the depth of an image (i.e. the area where chromium was retained on the chip should appear higher than the naked silicon surface). An image from the SEM is shown in Figure 9, where it appears that the area where the PMMA was etched retained the chromium coating. The indicates that this method has strong potential, with some tweaking, for successfully fabricating gold nanoparticles. However, these chromium areas were about 0.1 mm in width, 1 mm in length, and about 50 nm in thickness. This size and shape is not idea, but, again, the important thing is that this represents that the process does work. In an attempt to move closer to the desired nanoparticle size and shape, this manual etching process was repeated on a new chip, this time using the 0.05 mm diameter gold wire, in order to expose smaller areas. After using the same method as the larger wire, the chip was examined under the optical microscope. While this examination was not incredibly conclusive, there were small areas that appeared to be exposed when

the wire made contact with the PMMA. Chromium deposition was attempted on this chip, but at this point the deposition chamber failed to function. As this equipment malfunction occurred the day before this project had be finalized, no additional experimentation could be completed.

Discussion and Future Work

While ideal outcome of this project (successfully fabricating gold nanoparticles) was not accomplished, the question that motivated this study was answered. It was determined that field-induced atomic electrodeposition of gold onto silicon using an atomic force microscope is not feasible using the present set up in Bethel University's nanotechnology lab. Perhaps further study and development of a method that could work would be possible over the course of another semester, but given the present timeline and tools of this research, it could not be accomplished. Nevertheless, there were a few successes within the project. A method was developed for fabricating AFM tips that have the potential to be used for electrodeposition. Additionally, it was determined that the set up previously used for etching tungsten tips can be used to etch gold tips, albeit with some slight modification.
However, an alternative method with high potential for successful nanoparticle fabrication was developed. The PMMA etching-thermal deposition method proved to be feasible, even if nanoparticles were not successfully fabricated. To improve this method to actually make nanoparticles, all that is required is a better, more precise means of etching the PMMA, rather than the clumsy method of just contacting the surface with a large wire. Perhaps further experimentation with the AFM would lead to development of a successful etching method.
Another significant limitation of this method, which could be overcome in a more controlled setting, is that any minute dust particle, imperfection on the silicon chip, or bubble/impurity in the liquid PMMA solution causes (relatively) massive defects in the PMMA substrate. These defects make it nearly impossible to determine if the surface was successfully etched, as any small exposed areas are obscured by the much larger, more significant substrate defects. However, sub-mm areas of chromium were developed. Indicating that some tweaking of the process could yield nanoparticles.

Conclusion

This project proved to be rather challenging and somewhat frustrating. More than anything, it was a good experience learning the challenges of research and development when nothing seems to be working. The primary question of this project was answered, and an alternative method was developed. While the electrodeposition method was proven to be unfeasible at the present time, the PMMA exposure method was determined to be a viable option for nanoparticle fabrication.

References

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