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Fabrication of Tungsten Tips Suitable for Scanning Probe Microscopy by Electrochemical Etching Methods

Gobind Basnet
University of Arkansas, Fayetteville

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By

Gobind Basnet
Tribhuvan University
Bachelor of Science in Physics, 2000
University of Louisiana at Lafayette
Master of Science in Physics, 2009

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University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

Dr. Paul Thibado
Thesis Director

Dr. Jiali Li
Committee Member

Dr. Julia Kennefick
Committee Member

Dr. Jingyi Chen
Committee Member

ABSTRACT

The fabrication of metal tips is becoming an interesting field for scientists who are working in spectroscopy measurements. A significant amount of work has already been done in the tips fabrication process. Metal tips used to analyze the surface of materials play a key role in the scanning tunneling microscope (STM) technique. It's remarkable quality that it is used to study the surface of material at the atomic level.

There are various methods used in the tips fabrication process. Of diverse methods, three different electrochemical etching methods: submerged method, single lamella drop-off method, and double lamella drop-off method are commonly used to make various tips' shapes such as smaller cone shape, larger cone shape, sharp cone shape, and extremely sharp cone shape at room temperature are reported in this thesis. With submerged method, we made various tips in different etching parameters. The bulk surfaces of the etched tips were characterized using a simple optical microscope. Various tips shapes affected by etching parameters are discussed in this thesis. To better control tips' shapes, a single lamella method was used. However, the tips still etched when the lower part of the etching wire dropped because there was no auto cutoff etching circuit at the end of the etching process. Sometimes, this method produced non-cone shapes tips. To overcome this problem, a double lamella drop-off method was finally used. In this method, the various tips' shapes were made by the variation of the etchant height from the upper mark of the etch stop on the etching tungsten wire. The etch stop was enough to control the tips' shapes. The fabricated tips through various etching methods are recommended to study the surface of material in the STM chamber.

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LIST OF SYMBOLS

W tungsten wire

Pt platinum wire

Ir iridium wire

Pt-Ir platinum - iridium wire

WO_3 tungsten trioxide

OH^- hydroxide ion

WO_4^{2-} tungstate ion

H_2O water

e^- electron

E^0 overall standard electrode potential

$H_{2(g)}$ hydrogen gas

Cu copper

Au gold

Ta tantalum

LIST OF ABBREVIATIONS

STM scanning tunneling microscope

CG controlled geometry

$NaNO_2$ sodium nitride

HF hydrofluoric acid

NaOH sodium hydroxide

DC direct current

AC alternating current

NaCl sodium chloride

KCl potassium chloride

$CaCl_2$ calcium chloride

KOH potassium hydroxide

SOP standard oxidation potential

SRP standard reduction potential

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Nanotechnology, a field of engineering of functional systems at the molecular level, has attracted much interest in the past two decades. This field seeks to understand nanostructures which are made of nanoparticles. In order to understand mechanisms of nanostructures, considerable research efforts have been already applied in the fabrication of nanomaterial [01-04]. The most promising nanotechnology products can be found in nanomedicine, green nanotechnology, nanobiotechnology, energy applications of nanotechnology, industrial applications of nanotechnology, and potential applications of carbon nanotubes, etc. The major impact of nanotechnology can be especially seen on our quality of life. Therefore, the fabrication of nanostructures through various nanostructure patterns attracts many researchers working in diverse fields. They are using multiple methods for analyzing the fabricated nanostructures. In this thesis, the fabrication of tungsten tips via multiple methods will be discussed. Etched tips are recommended for analyzing the nanostructures' patterns at their atomic levels in scanning tunneling microscope (STM).

The scanning tunneling microscope was invented by Binnig and Rohrer in 1981 and then performed by Binnig, Rohrer, Gerber, and Weibel [05, 06]. This type of electron microscope is used to image the surface of the sample and study the electronic structure of the sample at its atomic resolution. The data collected in the STM chamber depends on the quality of vacuum, and the landscape of the sample. While these are important factors for the quality of STM images, the concept of STM is based on quantum tunneling. When a conducting metal tip is brought near the sample, a biased voltage applied between the tip and sample can allow electrons from the end of the tip to contact the nearest atom on the sample and produce a tunneling current which is a function of the local density of states of the sample, tip position, and applied voltage [07]. One of the crucial components of STM is the tip. The resolution and topographic images of the sample with the quality of the acquired data depend on the shape and sharpness of the tips as well as the electronic states of the tip. Therefore, the fabrication of tips has received significant attention in STM study. For atomic resolution images, a crucial first step is to fabricate a metallic tip which has an atom at its end position. In STM, most researchers use tips electrochemically etched from polycrystalline tungsten wire. Sometimes, multi-tips or blunt tips are produced during the fabrication of tips. For STM study, multi-tips [08] or blunt tips [09] are barely used. Additionally, the quality of STM images depends on the tip and sample. Therefore, the preparation of sharp tips with a low aspect ratio (tip length/tip shank) plays a key role for the quality of STM imaging during its scan over the surface. This kind of tip is required in the STM chamber to minimize its vibrations. Ideally, the tip is atomically sharp, but most of the tip preparation methods can not produce that kind of tip. Therefore, a tip has several asperities where the one closest to the surface is engaged for generating tunneling current.

STM tips are normally fabricated from non-reactive metals. Many non-reactive materials are proposed for STM tips [10], but tungsten (W) and platinum-iridium (Pt-Ir, 80/20) made from polycrystalline materials are the most commonly used. Among these materials, tungsten, which is cheap and easy to obtain, is a favorite material for making tips with a desired geometry due to its high melting point and high mechanical strength. In addition, the W tip, which serves as a suitable tip in the STM chamber, is highly applicable for taking quality STM images. In general, the typical diameter of the tungsten wire is 0.25 mm before etching, and the etched tip has a radius of curvature ranging 15 to 100 nm, a cone angle ranging from 10 to 60^0, and a total length of about 2.5 mm. The W tips are commercially available. Pt-Ir tips with high aspect ratio and controlled geometry (CG) are also commercially available to image deep trenches. These tips have a full cone angle from 15 to 80^0 with a tip radius of less than 50 nm and a total length of about 3 mm. In general, tungsten tips have more uniform shape than Pt-Ir tips. Currently, controllable ultra-sharp metal tips are commonly used in different fields as nanoelectronics, electron microscopy, nanolithography, and cell biology.

For more than 70 years, tremendous efforts and resources have been utilized to fabricate tips for better research and commercial purposes. This is a huge time period to explore tip fabrication technology. In 1937 Muller [11] stated that good tips have been made through electrochemical etching of tungsten and molybdenum wire in melted sodium nitride, $NaNO_2$ and for copper and nickel in nitric acid. In many laboratories, researchers have established their own laboratories for the fabrication of metallic probes. A huge number of works in a variety of methods for producing of sharp tips has performed. However, the high quality of the fabricated tips depends on the operators' experience in probe fabrication laboratories. Among the diverse methods in the fabrication of tips, the electrochemical etching [12 - 23] is one of the easiest, most practical, and most widely accepted methods to make inexpensive and reliable metallic probes with desired quality and reproducibility. Other advised techniques to prepare sharp tips are beam deposition [24-26], cutting [27], ion milling [28, 29], and others. Additionally, sharp tips with atomic resolution are manufactured by field evaporation, and characterized by field ion microscopy. However, we are not using field ion microscopy to produce metal tips, but we are able to produce sharp tips through standard electrochemical etching procedures. In each electrochemical etching process, the anodic dissolution of the metal electrode through the electrolyte takes place. The etching process has been typically utilized in two different ways as a direct current (dc) etching and an alternating current (ac) etching in order to control tips' shapes. In 1990, Ibe *et al.* proposed a dc electrochemical etching method for fabrication of tungsten tips with its controllable geometry, using an electronic cutoff circuit [15]. On the other hand, when fabricating tips by an ac etching, it is generally more difficult to control tips' geometry than dc etching [30].

In general, the tip fabricated from the dc drop-off method in which chemical etching takes place at the air/electrolyte meniscus is used in STM. With the drop-off method, the tip is formed when the lower part of the metal wire is etched away due to the larger force exerted by the weight of the lower part of the wire in comparison with the tensile strength of the etched tip. The dc etched tips have sharper shape than ac etched tips and the shape of a hyperboloid. The dc etched tips are generally used to take the higher resolution of scanning tunneling microscopy (STM). On the other hand, the same scenario has happened when the tip is etched through ac but the etched tip through ac has a conical shape.

In my thesis, three simple, inexpensive, and flexible electrochemical etching techniques: submerged method, single lamella drop-off method and double lamella drop-off method have been studied. They do not have a complicated mechanical setup, and an electronic cutoff circuit combines existing laboratory instruments with a safe electrolyte solution. These experiments involved in extensive research work in order to produce tungsten tips with a controllable tip profile under the varied etching parameters were performed in the Department of Physics, University of Arkansas Fayetteville. A commercial power supply was used to make tungsten tips with desired geometry via controlling the dc etching potential, dc etching current, and air/electrolyte meniscus levels. All of these methods performed under the same fabrication mechanism as the drop-off electrochemical etching method are successfully worked in obtaining controllable tips' shapes. One of the major concerns with tungsten tips during the etching procedure is that they have contaminants like etching byproducts such as tungsten trioxide WO_3, carbon, NaOH conglomerates and WO_3–Na microcrystals [31]. The thickness of the contaminants' layer seems to be ranged from a few nanometers to about 20 nm at the end of the tip [32]. While scanning the sample in the probe microscopy, the vibration of the tips needs to be minimized. It is possible only if the contaminants like etching byproducts or oxides are removed from the tips. Therefore, several cleaning procedures such as chemical treatment with HF [33], sputtering [34, 35], annealing [36, 37], using a low reverse voltage [38, 39], and etching when tips are vertically oriented downwards and upwards [40] are used to remove oxides and contaminants from the etched tips. One of the easiest ways which we used in this thesis for tip cleaning is a chemical operation process. In this process, the W tips are first washed with deionized water and then rinsed with ethanol and isopropanol after completing the etching process. The tips might still have an oxide layer. Finally, to obtain oxide-free tips, mineral acids are used. In our study, tips are whirled into 47% concentrated hydrofluoric acid solution for about 30 s. Finally, to characterize the etched tips, an optical microscope was used. From optical microscope' images under varied magnifications, one can compare the shapes of tips fabricated from the varied etching methods.

1.2 Research objective

The main goal of this research was to experimentally fabricate controllable metal tips such as tungsten tips which might play an important role in probe microscopy images. In order to obtain controllable tips, the appropriate methods had required to be researched at various levels. With this objective, different electrochemical etching methods were implemented. This thesis holds the detailed experimental explanation and corresponding results.

1.3 Motivation for research work

For the spectroscopy measurements, an easily controllable metal tip' shape is required. The tip can be fabricated using several methods. Each of them has played a key role in the fabrication process. However, our group focused on some of the experimental electrochemical etching methods: submerged method, single lamella drop-off method and double lamella drop-off method. The motivation behind this research was to provide a choice of methods which were easy in their experimental set up and cheaper then complex methods involved in tips fabrication process. Moreover, these experiments are motivated by the need to understand the physics and chemistry involved in the etching process.

1.4 Thesis outline

This thesis is organized into four chapters based on the electrochemical etching of tungsten wire. Chapter one is a brief introduction about the fabrication of metal tips which might be used in probe microscopy to test the quality of tips in further research work. Chapter two involves an overview of the experimental methods based on the electrochemical etching approach of tungsten wire in the electrolyte as an aqueous solution of NaOH. In this chapter, I discuss three well established electrochemical etching methods that are used to fabricate tips with controllable surface geometry and reproducible quality. The first is the submerged electrochemical etching method, one of the most well known methods which results in various tip shapes under varied dc potential applied through the electrodes. The second is the single lamella drop off method which results in tips with similar cone angle at a constant biased potential. This lamella method has become less popular than the submerged method. The third one, our group's original design, is an electrochemical etching method as a double lamella drop off method which results in various controllable tips' size and shape using partial etch stop (Nail Polish) tungsten wire. It is well reported that the etch stop plays a key role to shape the tips and then optimize the cone angles of the tips. An overview of the tip fabrication process from partial etch stop tungsten wire through this method is first discussed in section 2.2.3. Our group has investigated thoroughly the dependence of the tip geometry on the etching parameters. All of these methods are commonly used to etch the tips through non commercialized ways. Among these three methods, a double lamella method is extensively used in the fabrication of metal tips. The advantage of this method over the other two methods is that the fabrication of the tips does not require an electronic circuit breaker at the end of etching. Once the tip is etched, it is necessary to clean the surface of the etched tip and then characterize tip shape by its optical microscope image. Chapter three reports illustrative results of etched tips from the tungsten wire and corresponding discussion. I present the various shapes of etched tungsten tips with optical microscope images. Finally, I recommend some of the etching methods to produce tungsten tips suitable for the quality of STM images in this chapter. Chapter four provides a summary of the current research work, and also introduces possibilities for future work.

CHAPTER TWO

EXPERIMENTAL

2.1 Chapter Overview

This chapter provides an overview of electrochemical etching and varied experimental techniques with the instruments and materials which used to conduct research in this thesis. This chapter begins with a general introduction of electrochemical etching. In an effort to understand the tip fabrication in a sodium hydroxide (NaOH) aqueous solution, this chapter describes three different experimental methods: (1) a submerged electrochemical etching method, (2) a single lamella drop-off electrochemical etching method, and (3) a double lamella drop-off electrochemical etching method. At the end of the etching process, based on the optical microscope results reported, we tried to analyze the etched tips at their atomic level. However, there were difficulties to analyze the tips at this level. Therefore, we overviewed this work at the bulk level. In addition to knowledge gained of tip fabrication methods, this work can potentially create tips which might be used to take high quality images in scanning tunneling microscope (STM), but STM will not be discussed here because it is beyond the scope of this thesis.

2.2 Overview of electrochemical etching of a metal wire

Electrochemical etching is a reliable technique of producing sharp metal tips generally used in probe microscopy. Under the various methods of fabricating tips, "drop-off" method is a fast growing technique which is controlled via etching parameters and process. A liquid etchant is used to etch the metal wire in the "drop-off" method. The common way is to dip a metal wire into an electrolyte and then bias the wire through an ac or dc voltage so that electrochemical etching exits at the air/electrolyte interface which supports a thin layer of electrolyte meniscus. In our experimental setup for making tips, we had options to choose a biased voltage as either ac or dc. Using ac biased voltage, a large number of gas bubbles which disturb the etching process are produced around the wire [41-44]. On the other hand, with applying a high dc biased voltage, the wire is so quickly etched that the lower part of the wire drops off without fully developing the neck phenomenon in the wire [45]. Therefore, the low dc voltage is the best option for biasing the etching process. Moreover, the final shape of the tip depends on the meniscus surrounding the wire at the air/electrolyte interface, the concentration of electrochemical reaction, the types of metal, and the choice of the electrolyte. Generally, sodium hydroxide (NaOH) solution is used to make the tungsten tip. The tungsten wire is commonly used to make sharp tips, but contaminants and an oxide layer appear on the etched tips. To remove contaminants with oxide layer, different methods are implemented. However, we used chemical treatment method to solve this problem. On the other side, sodium chloride (NaCl), potassium chloride (KCl) or Calcium chloride ($CaCl_2$) are used for the fabrication of Platinum-Iridium tip. However, we did not make Platinum-Iridium tips in this thesis.

2.2.1 Experimental setup of submerged electrochemical etching method

The shape of the etched tip is one of the key characteristics for the quality of STM images. Researchers are using different tip fabricating techniques to control the cone angle as well as tip aspect ratio. In this thesis, it was necessary to find the major etching parameters which will affect the cone angle of the tip as well as aspect ratio. While finding the parameters, our group studied the effects of varying biased potential on the tips' shapes at a constant etching current during the etching process. A complete study of etched tip shapes via the varied biased potential at room temperature is reported in this thesis.

The submerged method is one of the most popular electrochemical etching methods that has been successfully used to make realiable metal tips. In the early 1990s, the submerged electrochemical method was developed to etch metal tips. The basic process of the submerged electrochemical etching method to fabricate metal tips is to vertically submerge a small diameter metal wire into an electrolyte solution so that the wire is electrochemically etched into a sharp tip due to the applied potential between anode and cathode. The main goal of this method is to decrease the diameter of the most common material, tungsten wire, from 0.25 mm to around 10 to 20 nm. This kind of tip is strongly applicable in taking high quality STM images. To perform the electrochemical etching process of tungsten wire, figure 2.1 below illustrates the schematic diagram of the tungsten tip fabrication system which was activated when a dc voltage between the anode and cathode was applied in a sodium hydroxide aqueous solution at the Department of Physics, University of Arkansas Fayetteville. By means of this method, all of the tips were etched at room temperature.

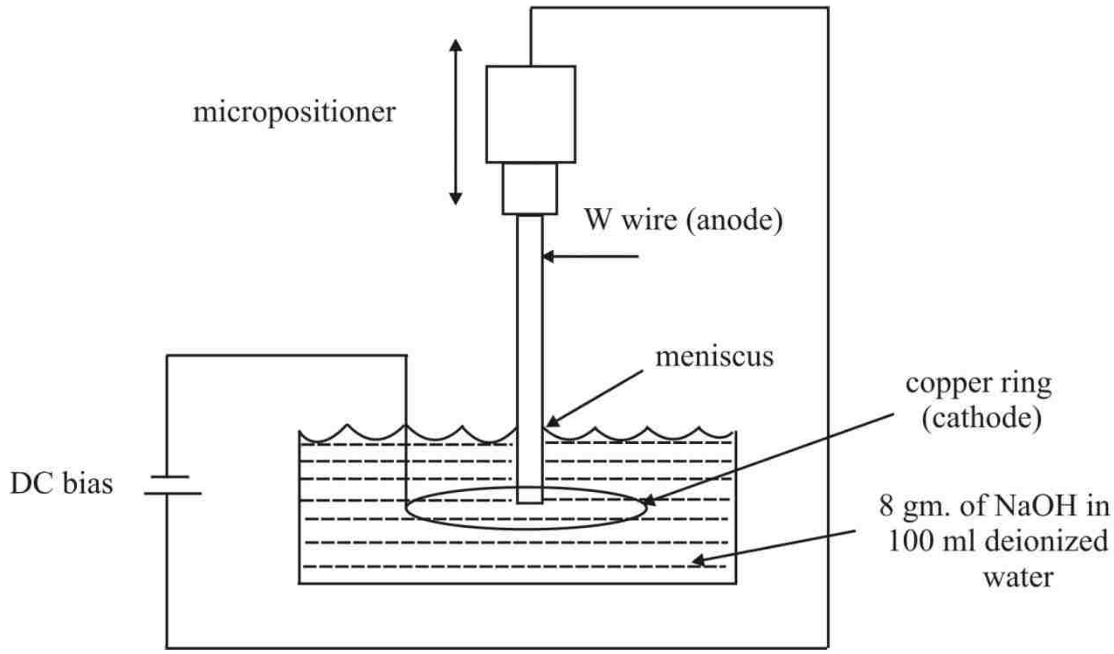

Figure 2.1: Schematic diagram of the submerged electrochemical etching system showing the submersion of a tungsten wire in a sodium hydroxide aqueous solution when a dc voltage is applied between cathode (copper ring) and anode (W wire) that drives the electrochemical etching process.

The etching system mainly consists of a copper (Cu) ring, a glass beaker, sodium hydroxide (NaOH) solution as an electrolyte, a dc voltage source, a tungsten (W) wire, an Omicron tip holder, a metallic stand for holding the tip holder, and a 30x magnification microscope. It was necessary to change the electrolyte after fabricating 10 to 12 tips through the same electrolyte for minimizing contaminants and oxides around the etched tips. The glass beaker and copper ring needed to be cleaned before using them in the etching process for reducing risk of contaminants. Generally, cleaning chemicals such as deionized water, ethanol, and isopropanol were used at room temperature. Figure 2.2 shows the photograph of the submerged electrochemical etching system. The negative pole of an Omicron dc power supply is connected to the copper ring with a copper wire of 0.85 mm diameter working as a counter electrode immersed in the etchant. The positive pole of an Omicron dc power supply is joined to the metal stand which holds metal tips with a micrometer screw on the top of the metal stand. A micrometer screw is used to measure the vertical motion of the W wire. The whole system is placed on a table to isolate the experimental setup from mechanical vibrations.

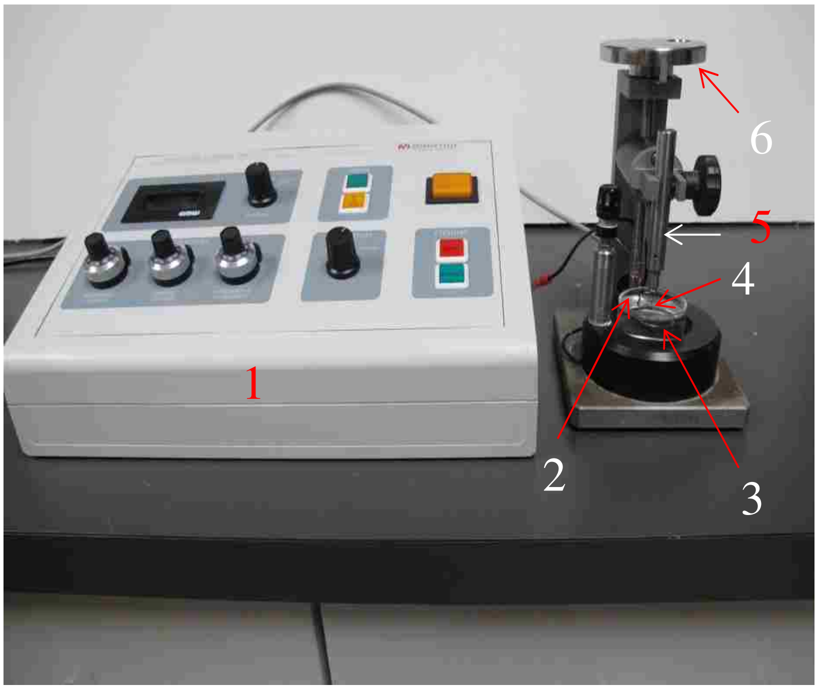

Figure 2.2: Submerged experimental electrochemical etching setup: omicron DC power supply (1), copper wire with its ring (2), electrolyte solution in the glass beaker (3), tungsten wire (4), magnetic metallic cylinder (5), and micrometer screw (6)

A tungsten wire which was a cylindrical shape of 0.25 mm in diameter was purchased in a quality with 99.95% purity from Alfa Aesar Company and came with a bundle of coil which was used to make the tips during the electrochemical etching process. From the coil of the W wire, a number of wire pieces were cut. Each piece was about 4 mm in length for convenience in the etching process. The Omicron tip holder held the W wire. As seen in Figure 2.3, the magnetic metallic cylinder attaches to a tip holder with a piece of tungsten wire and titanium wire.

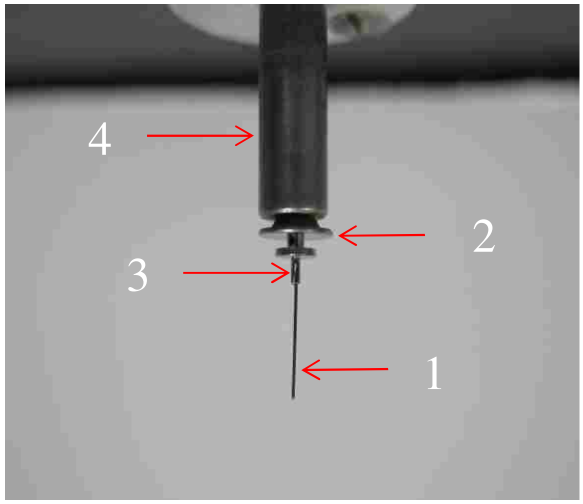

Figure 2.3 A digital picture of tungsten wire (1), tip holder (2), titanium wire (3), and magnetic metallic cylinder (4).

There are many parameters used to determine the etched tip shapes. One of the major parameters is the length of wire immersed into the electrolyte. If the submerged part of the wire is increased, the radius of curvature of the etched tip is also increased because of the growing weight of the wire below the air/electrolyte meniscus [15]. On the other hand, if the immersed part of the wire is small, it is difficult to make the neck just below the meniscus [46]. Without making a neck, there are no possibilities for making tips. In our work, we created an easily controllable metal tip shape when the submerged part of the wire was about 1.5 mm below the surface of the electrolyte solution. Initially, the tungsten wire was vertically directed in the middle of the copper ring with 15 mm diameter which was placed inside the glass beaker containing electrolyte solution, and a part of it passed through the center of the copper ring. In this experimental setup, the tungsten wire acting as an anode was connected with the positive pole of the power supply whereas the copper ring acting as a cathode was joined with the negative pole of the power supply. In order to measure the variation of tip shapes with the varied biased dc potential, Omicron power supply was used.

Generally, our group focused on the study of etched tip cone angle with tip aspect ratio at various biased dc potentials with a constant current during the etching process. During the tip fabrication process, we observed that the biased potential played a significant role in controlling cone angle size as well as aspect ratio of the metal tip. For example, for the same amount of etching current, the shape of the etched tips varied with changes in applied potential. On the other hand, the cone angle as well as aspect ratio of the metal tip was also depended on the electrolyte concentration. We are not going to focus on the role of electrolyte concentration during the etching of tungsten wire because it is out of our thesis's goal. Additionally, when the etching voltage was increased, the tips could be blunted on their apex because they were quickly etched before the formation of matured tips as well as further etching on the tips observed at the end of the fabrication process. At this moment, a medium range of etching voltage was favorable for the fabrication of tips when decreasing the additional etching during the cut-off time. The applied potential was varied from 3.5 V to 6.5 V at a constant etching current of 4 mA. The voltage and current applied across the electrodes were monitored frequently.

Once the tungsten wire was partially submerged into the electrolyte as shown in schematic figure 2.1 and the power was switched on, the etching process occurred at the air/electrolyte meniscus area. This area was monitored by a 30x magnification microscope (not shown in schematic diagram) which was in front of the tungsten wire. The intermediate steps during the etching process have been explained in section 2.2.1.1. At the end of the etching process, the lower part of the wire was dropped into the beaker and the upper part hanging on the tip holder became a tip. In order to stop further etching of the etched tip, the power supply was switched off right after the lower part of the wire dropped off.

2.2.1.1 Overview of the electrochemical etching reaction and etching process

The basic electrochemical reactions during the etching of tungsten wire can be explained as follows. When a DC voltage is applied through the electrodes, the electrochemical etching process starts over the immersed wire for which a number of side reactions are discussed by Ibe et al. [15]. The most common electrolytes which are used to etch the tungsten wire through the electrochemical etching process are potassium hydroxide (KOH) and sodium hydroxide (NaOH) [47, 48]. However, in our experiment, we freshly prepared an electrolyte as 8 g of NaOH in 100 ml de-ionized water to etch tungsten tips. During the electrochemical etching reaction, the anodic dissolution of tungsten wire takes place in aqueous base [49,50]. Though the overall etching reaction involved in the electrochemical etching process seems to be very simple, the real etching reaction is very complicated. The overall reactions involved in the electrochemical etching process are as follows:

At the anode : $$W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \quad (2.1)$$

Standard Oxidation Potential (SOP) = + 1.05 V

At the Cathode: $$6H_2O + 6e^- \rightarrow 3H_{2(g)} + 6OH^- \quad (2.2)$$

Standard Reduction Potential (SRP) = - 2.48 V

Total : $$W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_{2(g)} \quad (2.3)$$

Standard Electrode Potential (E^0) = - 1.43 V.

During the etching process, hydrogen bubbles $H_{2(g)}$ and OH^- ions as shown by equation (2.2) are produced on the cathode side whereas tungsten wire goes to tungsten anions WO_4^{2-} as represented by equation (2.1) through an oxidative dissolution process on the anode side. The sum of the standard oxidation potential (SOP) for tungsten in equation 2.1 and the standard reduction potential (SRP) for water in equation 2.2 is equal to the standard electrode potential (E^0) for the overall electrochemical reaction. Theoretically, tungstate anion is formed when E^0 exceeds 1.43 V. During etching, however, an applied potential higher than the standard electrode potential is essential because the resistance between the cathode and anode typically increases due to the process. For example, hydrogen which is produced during etching or changing the shape and size of the electrodes requires higher potential in comparison with E^0. When the etching process which is used for the fabrication of sharp tips starts over the total surface of immersed wire, it is essential that the electrochemical etching reaction is limited near the surface of the electrolyte solution. It is commonly known that the final shape of the tip depends on the shape of the meniscus formed by the electrolyte solution around the tungsten wire [15]. As shown in Figure 2.4a, as the tungsten wire is submerged into the electrolyte solution, the air/electrolyte meniscus is formed around the wire.

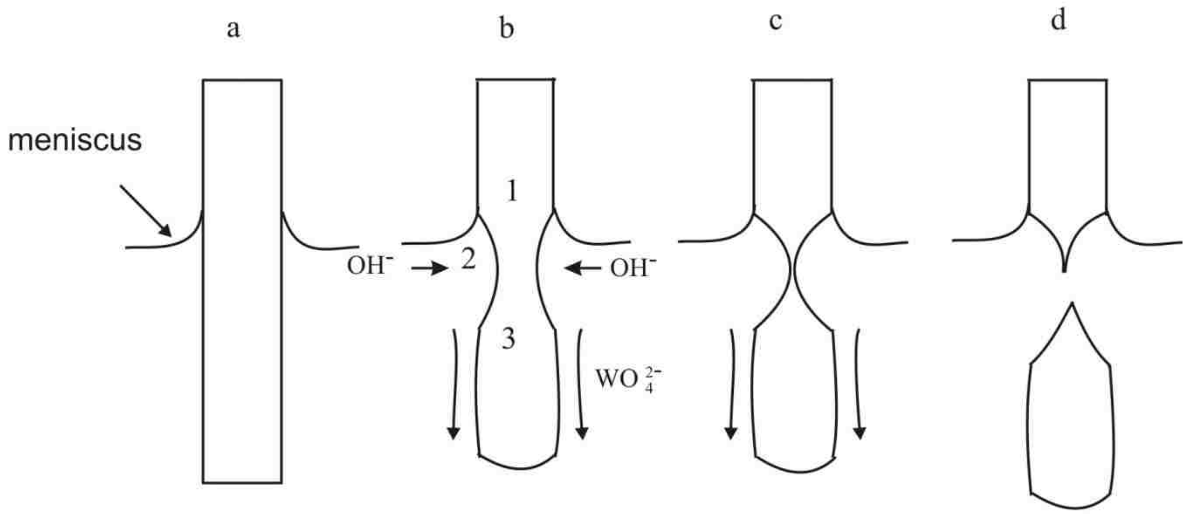

Figure 2.4: Schematic sequences of the etching mechanism. a) shows the formation of initial electrolyte meniscus. b) and c) illustrate the flow of tungstate ions (WO_4^{2-}) down the sides of W wire and OH^- towards the neck of the wire. d) shows the lower part drops off.

The OH^- ions produced during the etching process flow from the cathode electrode to the anode electrode. On the other hand, the etching of the tungsten wire generates soluble tungsten anions(WO_4^{2-}) as explained in equation 2.1. As shown in Figure 2.4b, the tungsten anions flow down to the lower end of the tungsten wire due to the flow of OH^- ions towards the wire and produce a thick layer around the lower end of the wire. The electrochemical etching rate decreases along the surface of the meniscus because the concentration of OH^- ions near the top of the meniscus position 1 in Figure 2.4b is lower than that of a major part of the solution. It is obvious from Figure 2.4b that the etching rate at the top of the meniscus is much lower than at the bottom region 2. Additionally, the layer of tungstate anions limits region 3 as shown in Figure 2.4b. As a result, a necking phenomenon occurs in region 2 which is just below the meniscus due to the maximum etching rate. After a certain time, the wire becomes so thin (Figure 2.4c) that the weight of the lower part of the wire does not balance with the tensile strength of the wire. As a result, the lower part of the wire finally drops because the tensile strength of the wire is lower than the weight of the lower part of the wire. The remaining part of the wire held by tip holder becomes a tip (Figure 2.4d). This method is known as a drop-off method [15]. In our experiment, we collected only the upper part of the etched tip which was considered as our final product. However, if we would like to consider the dropped lower part of the tungsten wire as our final tip, we must make a new experimental setup for the etching system which avoids the chances of collision between the container wall or the floor at the time of falling and the apex of the dropped lower tip. At the time that the tip drops, the upper tip apex continuously starts etching and its radius begins to increase if the voltage across electrodes is not immediately turned off. Hence, an important impact on the radius of the tip apex [51, 52, 53] occurs due to the time delay in turning off the voltage. In our current work, we used a power supply in which the applied voltage was continuously turned on after dropping the lower part of the etched tip, but we immediately removed the tips from the etching station to prevent further etching. Once completing the etching process, the tips were transferred to the cleaning station. At this station, the tips were washed first with de-ionized water and then with ethanol and isopropanol to remove any kind of contaminants and oxides. The washed tips might still have oxides. Finally, to remove the oxide layer, the tips were whirled in concentrated hydrofluoric acid (HF) for about 30 s. After cleaning, the etched tips were transferred to the optical microscope which was used to image the tips surfaces. The optical microscope is the simple way to identify the etched tips' shapes.

2.2.2 Single lamella electrochemical etching method

Numerous experimental methods are used to etch commercially available tungsten wire. However, this thesis realizes on this method, the single lamella drop-off electrochemical etching method, which is easy to setup for making sharp tips. We used this method to make metal tips used to study quality STM images. In this section, we will explain in detail how we designed our whole experimental set-up and then how it worked to make the tips. Finally, we will discuss the cleaning process of the etched tips and then analyze the tips' shapes through the optical microscope.

A typical schematic diagram of the single lamella drop-off system which was designed by our group for the electrochemical etching of the tungsten wire is shown in Figure 2.5. It comprised of a metallic ring, a glass beaker, sodium hydroxide (NaOH) with de-ionized water, a voltage source, a tungsten wire, and a tip holder for the W wire as in Figure 2.5. This experimental setting allowed us to independently control the etching system. One of the main aspects of this technique which distinguished it from the previous submerged technique was that, when the lower part of the tungsten wire was etched away, the upper part of the tip stopped further etching.

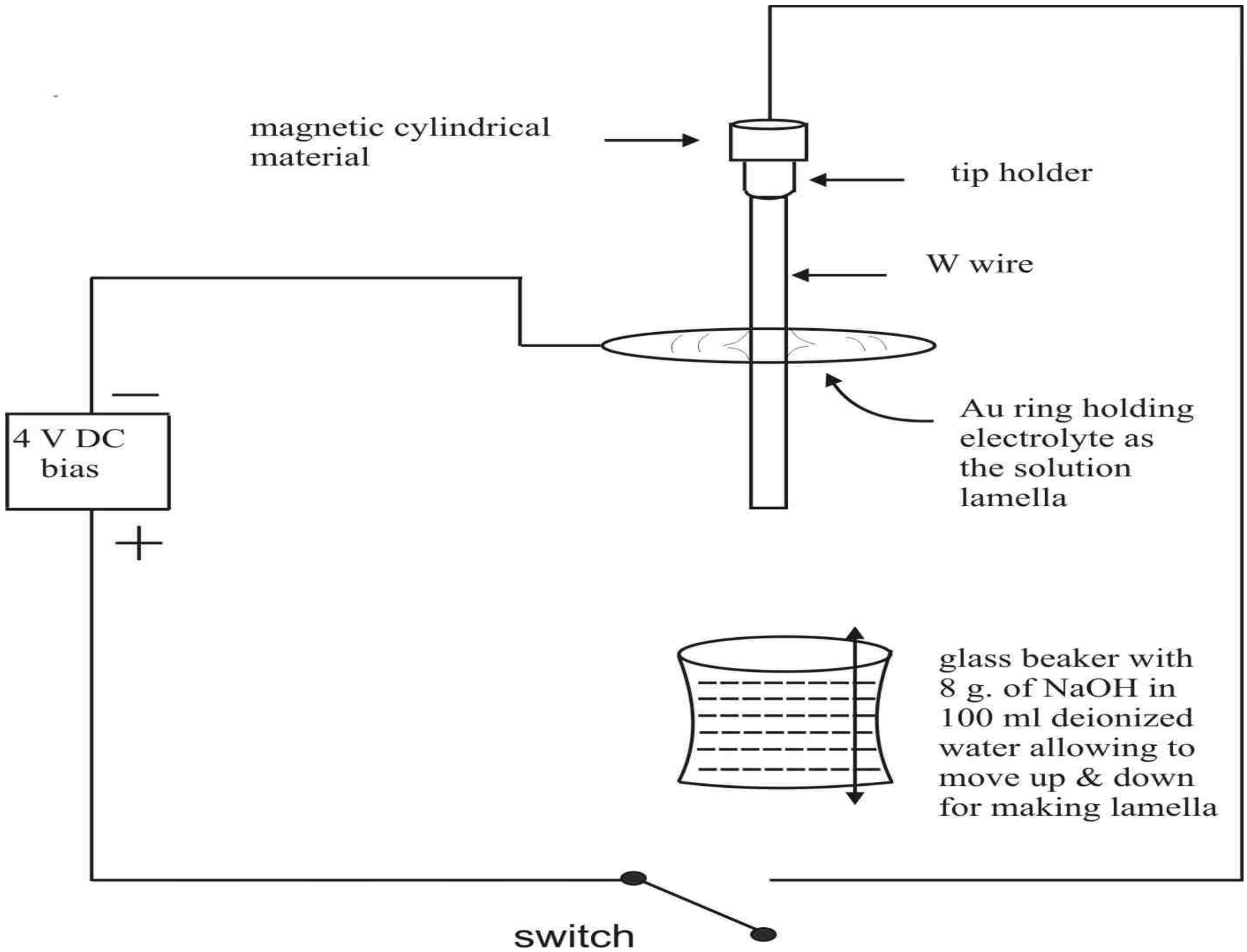

Figure 2.5 Experimental setup for the single lamella electrochemical etching system during the preparation of the tungsten tips. The etching process will start when the biased potential is applied across the ring and tungsten wire. The gold ring carries the electrolyte solution. At the end of the etching process, the lower portion of the wire drops and its upper portion acts as a final tip.

The magnetic tip holder served as a holder for a piece of tungsten wire of 0.25 mm diameter and 8 mm length. The exact length of the W wire was not critical. However, we chose this length to avoid premature breaking effect in the tungsten wire. Initially, a piece of tungsten wire was inserted into the Omicron tip holder and then supported by a piece of titanium wire which was also inserted in the same holder. The holder was attached to a piece of the magnetic cylinder. The vertically aligned W wire was passed through the center of the gold ring of 15 mm diameter and 0.90 mm thickness in a perpendicular position to the horizontal plane of the ring. The negative terminal of the Keithley 2400 SourceMeter as a constant voltage power supply was then connected to the suspended gold ring acting as the counter electrode during the etching process, while its positive terminal was joined to the W wire represented as the working electrode. The beaker just below the ring, as shown in Figure 2.5, was then filled with the etching solution: 8 g of NaOH in 100 ml distilled water. To activate the etching process, a small biased potential of + 4 V was applied to the tungsten wire and the gold ring. The gold ring was immersed into the etchant. As a result, a thin film of the electrolyte solution in which the etching process began was suspended in the gold ring via its surface tension and viscosity. The ring could be moved along x-, y- and z-directions via micromanupulators attached to the experimental etching set-up. The meniscus's position was determined by the local ion (OH^- and WO_4^{2-} ion) density distribution.

During the etching process, we observed bubbles along the thin layer of the meniscus. Additionally, the bottom surface of the lamella gradually fell in a downward direction because the density of the electrolyte at the lower part of the wire from the meniscus position was increased [15]. The overall electrochemical redox reaction can be described as follows:

$$W(\text{solid}) + OH^- + 2\,H_2O \longrightarrow WO_4^{2-}\,(\text{anode}) + 3\,H_2\,(\text{gas, cathode})$$

Where E^0 = - 1.43 V.

In the etching process, the reaction is complicated because intermediate oxidizing steps occur [15]. While the OH^- ion concentration decreases, the WO_4^{2-} ion concentration increases. Therefore, the overall film of the meniscus saturates. These effects will change the etching reaction rate. In our experiment, the decreasing etching reaction rate was observed when the etching current was decreased with the increasing time. The whole etching time to make a tip was about 30 min. During the etching process, the meniscus's film sometimes broke up. At those times, a new film of the electrolyte supported by the ring was again required. Therefore, we moved a glass beaker containing the electrolyte vertically until the ring submerged into the electrolyte and then the beaker was moved back. This step was continued until making the final tip. To monitor the electrolyte meniscus around the wire, the 30x magnification microscope (not shown in the schematic diagram) was used.

When the etching process ended, the upper part of the W wire was hanging in the tip holder and the portion of W wire below the lamella dropped into the beaker because the weight of the lower part of the W wire then exceeded the tensile strength of the etched tip. The remaining part of the W wire left on the tip holder became the final product of the etching process. Right after the drop-off, it was necessary to remove the contaminants as well as thin oxide layer from the etched tips [15, 49, 50] before using them in the scanning probe microscopy. There were many techniques used to remove the etching residues from the tips. One of the easiest ways which we used in our lab was the chemical operation process. In this process, the tips were rinsed off with DI-water, ethanol, and isopropanol in sequence to remove the contaminants and oxides. Finally, the tips were cleaned by partially dipping them in the concentrated hydrofluoric acid for 30 s. Right after cleaning, the macroscopic shape of the tip was examined in the optical microscope.

2.2.3 Double lamella drop-off electrochemical etching method

Currently, researchers are using the expensive and elaborate electrochemical etching methods for the fabrication of tips. Our group is interested in modifying one of the electrochemical etching methods through a simple and inexpensive way. Although the initial idea of fabricating metal tips via the double lamella drop-off electrochemical etching method was first explored [54] in early 2003, presented here is a modified form of this method which is used to make tips from tungsten wire at room temperature.

In the previous studies of the double lamella drop-off etching method, it was found that tips were fabricated without using the etch stop (nail polish) coating on the metal wire. In this thesis, the etch stop only partially coated the tungsten wire used to make the tips. This method utilized a simple etching method for the fabrication of the tips in comparison with the other fabrication methods. This method was simply a modified form of a single lamella drop-off etching method which introduced an additional gold metal ring working as an electrode. Although this approach is not a standard method for producing a large volume of metal tips in the industry, it has found a wide range of use in the research field. The experimental setup of our double lamellae drop-off etching method is schematically shown in Figure 2.6(a).

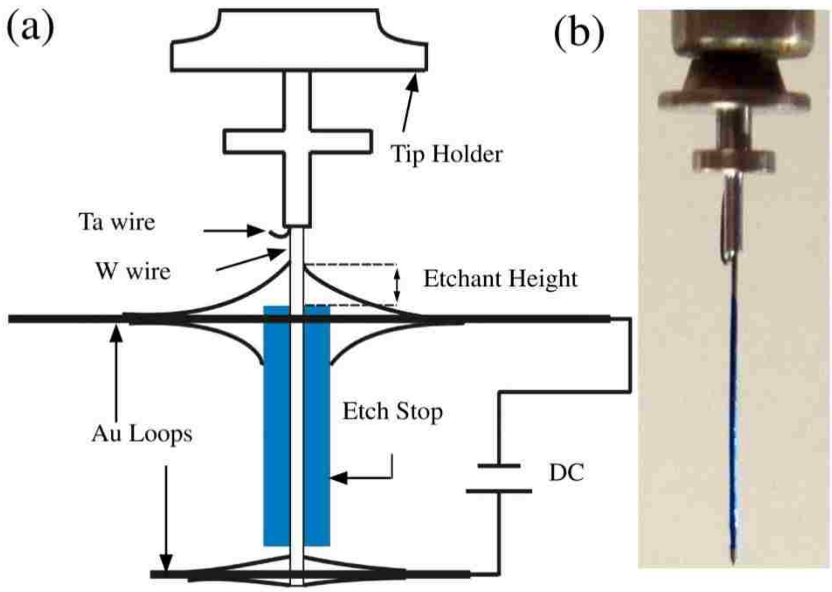

Figure 2.6. The modified double lamella drop-off electrochemical etching system: (a) Schematic view of a double lamella dropoff electrochemical etching experimental setup. The partial etch stop (nail polish) tungsten (W) wire inserted into an Omicron tip holder with a few mm in length of tantalum (Ta) wire, which supports the tungsten wire at the tip holder, is vertically oriented. The upper gold ring is connected to the negative pole of the power supply whereas the lower gold ring is connected with the positive pole of the power supply. Both rings support the drops of NaOH solution to etch the W wire. (b) A digital picture of a partially coated etch stop W wire with a piece of Ta wire both inserted into the tip holder and a piece of cylindrical magnetic material.

The main components of the etching apparatus consist of two gold (Au) rings, a glass beaker, an electrolyte as sodium hydroxide (NaOH) solution, a voltage source, a tungsten wire, a tantalum wire, etch stop (nail polish), an Omicron tip holder, a metallic stand for holding the tip holder, and a 30x magnification microscope. The tungsten wire of 0.25 mm diameter and 8 mm length was cleaned in ethanol before using it in the etching process. The wire was vertically inserted into the tip holder with a piece of Ta wire of 4 mm length and 0.15 mm diameter which was used to hold the W wire in the tip holder. A piece of the cylindrical magnetic material, as shown in the upper part of Figure 2.6 (b), was used to hold the tip holder. Prior to partially dipping the tungsten wire in the etchant, the surface of the W wire was partially coated by a 0.05 mm thick film of the etch stop to control the tips' shapes. We left 0.5 mm uncoated at the buttom of the wire and 3 mm at the top, with the midsection coated in etch stop. The expected thickness of etch stop was almost the same for all tungsten wires in this work. The surface of the etch stop coated on the tungsten wire can be seen in Figure 2.6 (b). Since the very end of the W wire was uncoated, the d.c. current flowed through the etching circuit. The most important thing was that the etch stop needed to be dryed before starting the etching process. For the drying purpose of the etch stop, the W wire was annealed for 15 seconds by an UNGAR 1095 dual temperature heat gun which was placed about 50 cm away from the wire because it provided high performance and flameless heat.

Initially, the W wire to be etched was passed through the center of the bottom and top gold rings (schematically shown in Figure 2.6 (a)) which were separated at about 4.5 mm distance in horizontal, parallel alignment. For cleaning purposes, both rings were placed in a glass beaker containing in-house de-ionized water at room temperature for about 5 minutes. Right after that, the rings were cleaned with methanol. The W wire was positioned at the focal point of the 30x magnification microscope as shown in Figure 2.7 (2). A constant dc power supply of 8 V from a Keithley 2400 sourcemeter (shown in Figure 2.7 (4)) to construct the feedback control was applied between the upper ring connected to the negative end of a power supply and the lower ring joined to the positive end of a power supply until the wire became a tip. The positions of the rings along x, y, and z directions were adjusted using micromanipulators as shown in Figure 2.7 (6, 7 & 5).

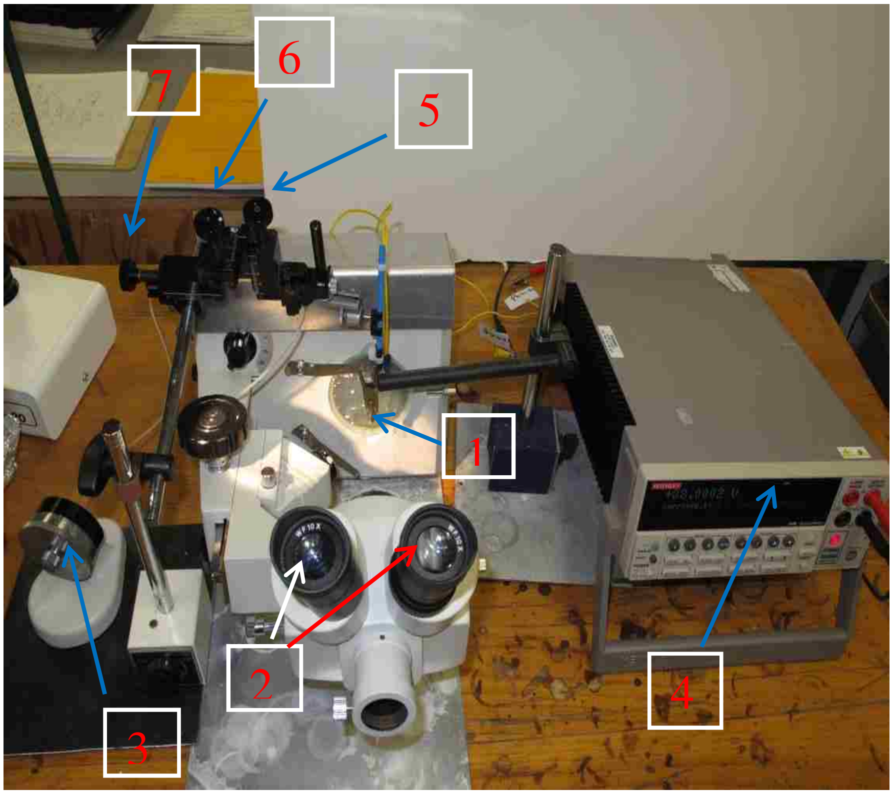

Figure 2.7: A picture of a double lamella electrochemical etching system (Image source Uark-Phys. Lab.). The tungsten wire inserted into the tip holder which is attached with a magnetic cylindrical material (1) is passed through the two gold rings which positioned parallel along horizontal plane. The position of the wire is monitored by the 30x microscope (2). A micrometer (3) controls the air/electrolyte meniscus held via the rings' movements. The power supply, the Keithley 2400 sourcemeter (4), is used to power up the etching process. The distance of the upper ring and lower ring from the tip holder can be measured from z-scale of the micromanipulator (5) attached to the tip holder stand. In addition, the x- and y- directional motions of the W wire with rings are controlled by two other micromanipulators (6 and 7).

In our study, the etchant used to activate the etching process was a solution of 8 g of sodium hydroxide in 100 ml deionized water. The electrolyte solution was taken in a glass beaker and then moved along the vertical direction to a position at which both gold rings submerged in the electrolyte. As the beaker was moved down, each ring held an etchant lamella. The etching of the tungsten wire started when both rings held the air/electrolyte interface meniscus and a power source was turned on. At the same time, the etching current was monitored with the Keithley 2400 sourcemeter. The electrochemical etching was observed over the two positions of the wire surrounded by the air/electrolyte meniscus. Sometimes, the upper lamella broke up during the etching process because the tungstate ions (WO_4^{2-}) formed at the upper gold ring. This happened many times during the fabrication of a single tip. Each time, we redipped the gold rings in the etchant to form a fresh lamella on the rings. A number of the side reactions involved were discussed by Ibe et al. [15]. During the electrochemical etching reaction, hydrogen bubbles H_2(g) and OH^- ions were produced on the cathode side whereas the W wire changed to W anions through the oxidative dissolution process on the anode side. Since a large number of hydrogen bubbles and ions were produced in the lower meniscus, they disturbed the etching of the W wire. Meanwhile, on the surface of the upper meniscus, fewer bubbles and ions were observed because some of the bubbles and ions might flow from the cathode to the anode through the W wire. Due to the anions produced at the anode end, the tungsten wire was continuously etched through the meniscus in the upper ring. After a short period of etching, a necking shape in the W wire appeared. As the potential was continuously applied, the necking part became so thin that the lower part of the W wire dropped from the upper ring due to gravity, and the upper part left on the tip holder became the final product of the etching process. At the end of the etching process, the current became zero, but the applied dc potential was still the same as the initial applied potential. No more etching was seen at the remaining part of the tungsten wire. After the termination of the etching, each tip was taken out of the magnetic cylindrical support. Before the etched tips were analyzed, the W tips were immediately rinsed with deionized water to prevent the etched tip from further oxidation and finally with ethanol and isopropanol to remove the remnants of the etchant. The tip might have still an oxide layer. To remove the remaining oxides from the tip, we whirled the tip in concentrated hydrofluoric acid for around 30 s. Finally, the shapes and aspect ratio of the etched W tips were characterized using their optical microscope images.

With the process as described above, we fabricated more than 60 tungsten tips. The microscope (shown in Figure 2.7(2)) was used to monitor the tungsten tips which was affected by the etchant height measured from the upper mark of the etch stop on the W wire. Initially, we leveled the etchant height of about 0 mm from the upper mark of the etch stop. At this level, we made more than 20 tips and tried to control the tips' shapes, but we found all of the etched tips in the non cone shapes. In order to improve the tips' shapes, it was important to continuously change in the meniscus level until getting the different tips' shapes as compared with the previous tips' shapes. Again to make a better cone angle tip's shape, we moved to a new meniscus level as 0.3 mm etchant height. At this level, we made 20 tips to examine their apex shapes. Furthermore, we fabricated 20 more tips at about 0.6 mm etchant height and then examined their shapes using the optical microscope.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Chapter overview

The objective of the extensive experimentation performed in this thesis was to control the mechanism of the experimental etching setup with the various etching parameters, understand the physics principles behind this mechanism and then finally fabricate tungsten tips in this mechanism. All tips investigated were etched at room temperature in the Department of Physics, University of Arkansas Fayetteville via electrochemical etching methods. This chapter includes the results obtained from three electrochemical etching methods: submerged method, single lamella drop-off method, and double lamella drop-off method which were discussed in chapter two. To analyze the etched tips, the optical microscope was used. The various images of the tips which were etched under the varied etching parameters, taken from the optical microscope are presented in the following three sections.

3.2 Results and discussion from submerged method

In this section, the results of the submerged electrochemical etching method over the varied etching parameters which were discussed in the previous chapter, are presented. Generally, this section provides results including the effect of biased potentials which were applied between the working electrode and the counter electrode at room temperature with a constant dc etching current. More than 100 tungsten tips were etched by the submerged electrochemical etching method which worked at a constant dc current and the varied biased potentials. The surface of the etched tip was imaged via the optical microscope.

As discussed in chapter two, when E^0 exceeded 1.43 V, the electrochemical etching of metal wire might take place [15]. The actual value of E^0 might be varied slightly depending on the experimental setup. From Ibe et al. [15], we concluded that a dc voltage choosen in the range of 3.5 to 6.5 volts was favorable for the fabrication of the controllable tips. In our experiment, tungsten tips were fabricated in the varied biased potentials as a low etching voltage of 3.5 V and a high etching voltage of 6.5 V for examining the affect of potentials on the cone angle as well as aspect ratio of the tips. At a high dc etching voltage of 6.5 V, more than 20 tungsten tips were fabricated. About 85% of them had extremely sharp cone shapes. Only about 15% of them had smaller cone shapes. With a low dc etching voltage of 3.5 V, we made more than 20 tungsten tips. Among them, we found that 80% had a smaller cone shape and 20% a bigger cone shape. Similarly, more than 40 tungsten tips were fabricated at the biased potentials of 4.5 V and 5.5 V respectively. It was found that around 80% of the etched tips at the potential of 4.5 V had a bigger cone shape and around 85% of the etched tips at the potential of 5.5 V a smaller cone shape respectively. In other words, the sharpness of the tips was directly proportional to the applied potential after the biased potential of 4.5 V. On the other hand, due to the decrease in the biased potential from 4.5 V to 3.5 V, the cone angle of the etched tip was also decreased. At that time, we also analyzed the aspect ratio of the etched tips. We found that most of the tips had the varied aspect ratio when the biased potentials were increased to etch the tips. Thus, when the biased potential was changed, both the sharpness and aspect ratio of the etched tips were changed. From this discussion, it was found that the bigger cone shaped tip at the applied potential of 4.5 V was consistent with previous studies [55].

To better understand the results of the varied etched tips' shapes as discussed in the previous paragraph, we need to focus on the etching mechanism. When the W wire was dipped in the electrolyte, an air/electrolyte meniscus was formed around the wire due to the surface tension and viscosity of the electrolyte solution. During the formation of the necking shape on the W wire which was observed just below the air/electrolyte meniscus, a non-uniform etching rate along the W wire was observed. The extent of the necking phenomenon on the interface depended on the rates of reaction products along the wire surface [56]. This might be due to the non-uniformly distributed concentration of OH^- ions along the W wire which was dipped in the electrolyte solution. The concentration just below the top of the meniscus was lower than that of the solution surrounding the wire due to the lower number of OH^- ions transferred to the wire. The second reason was that bubble density was increased from the tip apex to the meniscus. The third reason was that the rate of diffusion of OH^- ions to the top of the air/electrolyte meniscus was slower than that to the bottom and producing a concave shape at the etchant level during the electrochemical etching [15, 57]. The fourth reason was that the tungsten anions (WO_4^{2-}) which flew down along the wire [15] accumulated at the lower part of the wire as well as the current density of electrochemical reaction was dependent on the concentration of OH^- [58]. Moreover, at the high etching voltages, the presence of vigorous bubbling stream resulted in a less controllable tip profile and increased irregularities in the tip profile observed. When the initial applied voltage was greater than 4.5 V, irregularities in the tip profile were observed. On the other hand, if the applied potential was lower, it might result in a lower number of more random flow of OH^- ions to the W wire. In addition, the diffusion of the OH^- ions across the bubbling stream around the wire became slower. As a result, the etching rate at the lower portion of the wire was much slower then the resulting tip at the upper portion of the wire. Finally, the shape of tips was also depended on how often the refereshed electrolyte was used to etch the tips. In our research work, we used same electrolyte solution for making 10 tips. All of these facts lead to make the varied cone shaped tips.

Some of the randomly selected optimized optical images of typical etched tips fabricated at the applied dc etching voltages of 3.5 V, 4.5 V, 5.5 V and 6.5 V with a constant dc etching current of 4 mA and a fixed concentration of 8 g of NaOH in 100 ml deionized water are illustrated in Figure 3.1. Figure 3.1 shows the dependence of the tip apex radius to the effective applied dc etching voltages. When the etched tip was analyzed using the optical microscope, each tip was observed at three different magnifications: x10, x50 and x100.

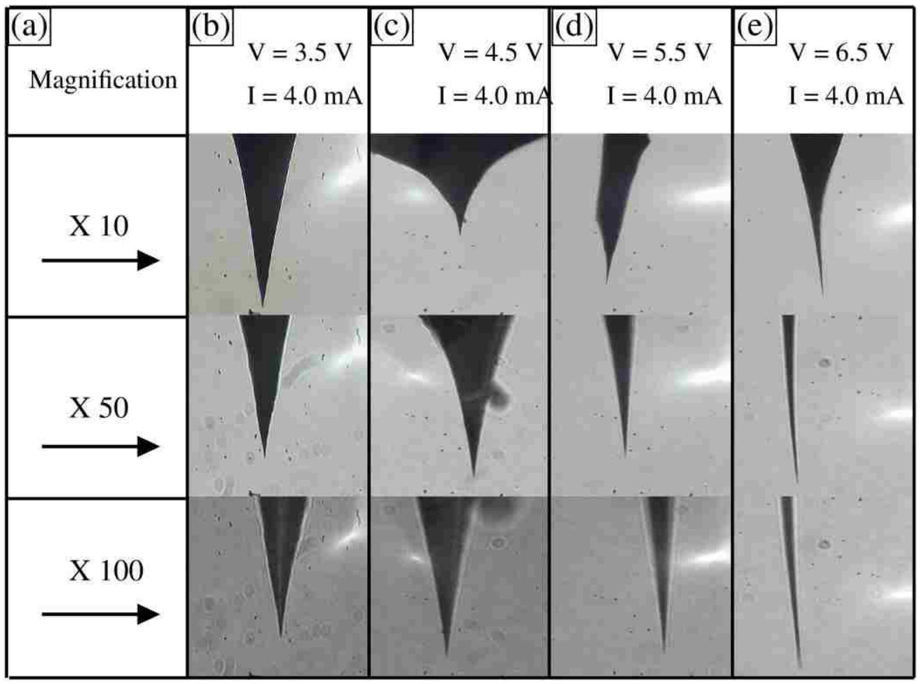

Figure 3.1 Optical microscope images at three different magnifications as x10, x50 and x100 of the tungsten probes fabricated via submerged electrochemical etching method under different etching conditions with fixed concentration of 8 gm of NaOH in 100 ml deionized water: (a) showing the values of magnification (b) dc bias voltage 3.5 V, dc etching current 4.0 mA, etching time 33 min; (c) dc bias voltage 4.5 V, dc etching current 4.0 mA, etching duration 27 min; (d) dc bias voltage 5.5 V, dc etching current 4.0 mA, etching time 23 min; (e) dc bias voltage 6.5 V, dc etching current 4.0 mA, etching duration 18 min. The images of the etched tip in each column were observed at low to high magnification from top to bottom.

The second to fifth column except the first row in figures 3.1 represent the optical microscope images of the tungsten tips etched under the applied dc voltages of 3.5 V, 4.5 V, 5.5 V and 6.5 V respectively at a fixed dc etching current of 4 mA. The etched tips at three different magnifications as X 10, X 50 and X 100 are presented from second to fourth rows in figure 3.1 respectively. The corresponding dc etching duration was varied due to the etching of the tungsten wire at varied potentials. In Figure 3.1, we could find that the sharpness of the etched tip increases as the applied voltage is increased behind 4.5 V. In other words, with an increase in the applied potential above 4.5 V, the cone angle of the etched tip decreased as in Figure 3.1 due to better directing the flow of OH^- ions towards the W wire, giving rise to etching rate [59]. On the other hand, it is also seen from Figure 3.1 that the sharpness of the etched tip also increases as the applied voltage is decreased from 4.5 V. This result favors the work done by Kim et al. [55]. Thus, comparing the cone angles of the tips in Figure 3.1 advised that a tungsten tip with a bigger cone angle as shown in the third column of figure 3.1 was produced through an etching process at a medium ranged applied voltage of 4.5 V and an etching current of 4 mA. Table 3.1 shows some information about the etching method. Normally, the submerged electrochemical etching parameters with summarized results of etched tip are listed in this table.

Corresponding figures	DC Volt (V)	Current (mA)	Etching duration (min)	Etched tip's shape
Second column of Figure 3.1	3.5	4	33	Smaller cone
Third column of Figure 3.1	4.5	4	27	bigger cone
Fourth column of Figure 3.1	5.5	4	23	sharp cone shape
Fifth column of Figure 3.1	6.5	4	18	extremely sharp cone shape

Table 3.1: A summary of the dc biased voltage, dc etching current, etching duration and etched tip's shapes during etching process. All tips were fabricated at room temperature in the Department of Physics, University of Arkansas Fayetteville.

Alternatively, some of the tungsten tips were also fabricated under a varied dc etching current with a constant dc potential. With an increase in the dc etching current as 3 mA, 4 mA, 5mA and 6mA, there was no significant improvement in the yield of tips etched under an effective dc etching voltage of 4.5 V. All of the tips almost looked like same cone shape with the same aspect ratio. From the results as discussed in this chapter, making tips with the varied biased potentials at a constant dc etching current was more favorable to control the cone angle as well as the aspect ratio of the etched tips. Thus, the optimum level of the dc etching voltages needs to be selected in such a way that it can fabricate the W tips with controllable shape.

3.3 Results and discussion from single lamella method

This section discusses the tungsten tips etched using a single lamella drop off electrochemical etching method in detail. Our study focused on the control of the tips shapes during the fabrication of tungsten tips under an experimental method as explained in the previous section 2.2.2. The controlling of shapes was one of the most challenging issues for researchers who had shown many research efforts during the fabrication of tips. Many investigations had focused on the fabrication and characterization of the tip during etching. To produce controllable tips, a biased potential of 4.5 V which was one of the effective etching parameters was applied across the electrodes during electrochemical etching at room temperature because an applied potential higher than standard electrode potential E^0 in Eq. (2.3) needed to overcome the resistance between the anode and cathode typically increased due to the applied dc voltage and dc etching current. Since we found an optimized cone angle of the etched tip at a biased potential of 4.5 V in submerged electrochemical etching method, we chose an electrical potential of 4.5 V to etch the tip during a single lamella drop-off electrochemical etching method. Under these parameters, more than 30 tips were fabricated. The etching duration of each tip was about 30 min. To analyze the overall shape of etched tips, one of the frequently used approaches, namely the optical microscope, was used. In our study, we found that 80% of the etched tips had bigger cone shape and 20% of them a smaller cone shape. The reasons behind these facts have already been addressed in the previous section 3.2.

Figure 3.2 shows some of the randomely selected optimized optical microscope images of the tips fabricated at the room temperature at three different magnifications: x10, x50 and x100 respectively. It is obvious, as seen in Figure 3.2, that the tips' images illustrate that all tips in each row have a similar cone shape with a smooth surface area and have comparable cone angles. In other words, from the optical microscope images of etched tips illustrated in Figure 3.2, one could obviously observe that there is no significant difference in the tips' shapes. Therefore, these optical images confirmed that the etched tips had well-defined cone shapes at a biased potential of 4.5 V.

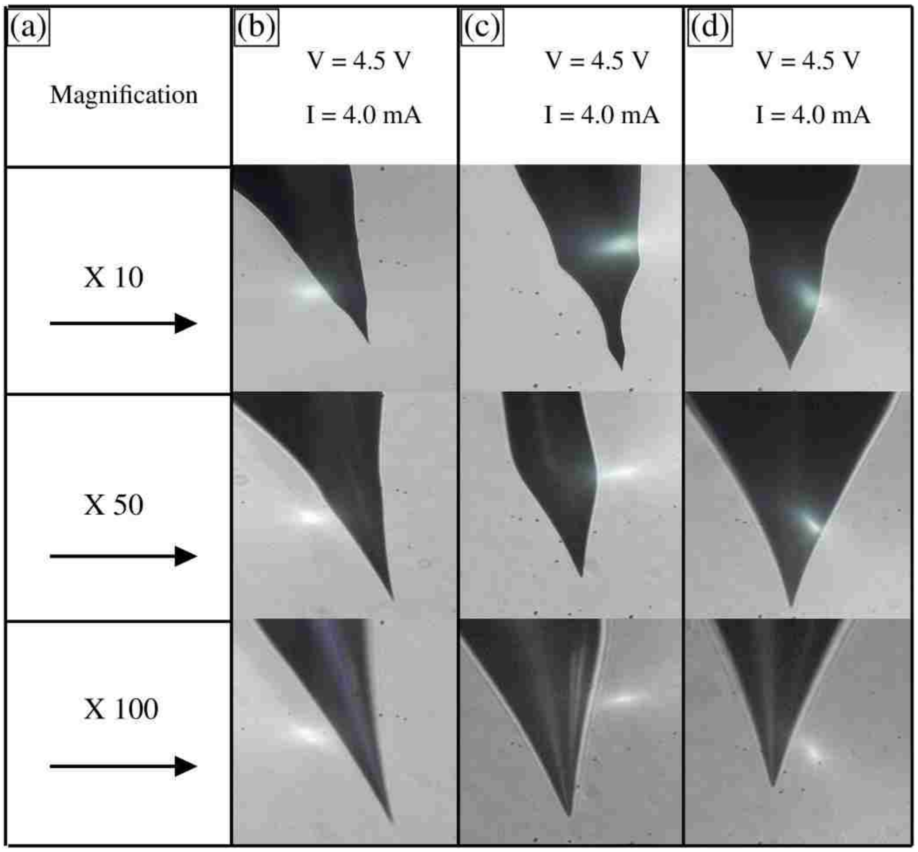

Figure 3.2 Optical microscope images of some of the optimized cone angle tungsten tips at three different magnifications: x10, x50 and x100 fabricated via single lamella drop off electrochemical etching method under similar etching conditions as a dc biased potential of 4 V and a dc etching current of 4.0 mA. The images of the etched tip in each column are displaced from low magnification: x10 to high magnification: x100 from top to bottom. In this figure, each row staring from second has similar cone shaps images of tips.

Sometimes, the etched tips were asymmetrical in shape using this method. There were some excellent features supported by the asymmetrical tip shape. Some of them which were discussed earlier in this chapter could support this fact. However, there were still some reasons proposed via our research group which might be convenient to deal with the asymmetrical tip shape. First, the tip making wire might not be vertically-aligned on the horizontal plane of the gold ring. Therefore, we needed to be careful about the alinement of the tungsten wire's position through the ring. Otherwise, non vertically-aligned wire possessed some none cone shape features. Second, the wire which was attached to the metal tip holder might not be vertically positioned in the z direction through the center of the ring. This led to twisted tips shapes. Most importantly, the surface tension of the vertically aligned wire might not be uniformly varied and consequently supported the non cone tips during etching. .

3.4 Results and discussion from double lamella method

All of the work discussed here is used for producing the controllable etched tip. In order to achieve the controllable etched tip, a double lamella dropoff electrochemical etching method as discussed in chapter two was utilized. The focus of this section was that the effect of varied etchant heights from the upper mark of etch stop on the tungsten wire affecting the tips formation was reported. We made more than 60 tips under the three different etchant heights as about 0 mm, 0.3 mm and 0.6 mm from the upper mark of the etch stop on the tungsten wire at room temperature in this method. To evaluate the bulk surface features of the etched tips, the tips were imaged using the optical microscope. Some of image results have been presented in this section. All the optical microscope images shown in this section have illustrated the cone size distribution of fabricated tips with varied etchant heights. It is obviously seen from the optical microscope images of the etched tips in Figure 3.3 that the etch stop is enough to produce the varied tips shapes.

To study the effect of the etch stop during tips fabrication, the varied etchant heights from the upper mark of the etch stop affecting the tips' cone angles were analyzed. During the period of analysis using the optical microscope, the tips were imaged at three different magnificatios: x10, x50 and x100.

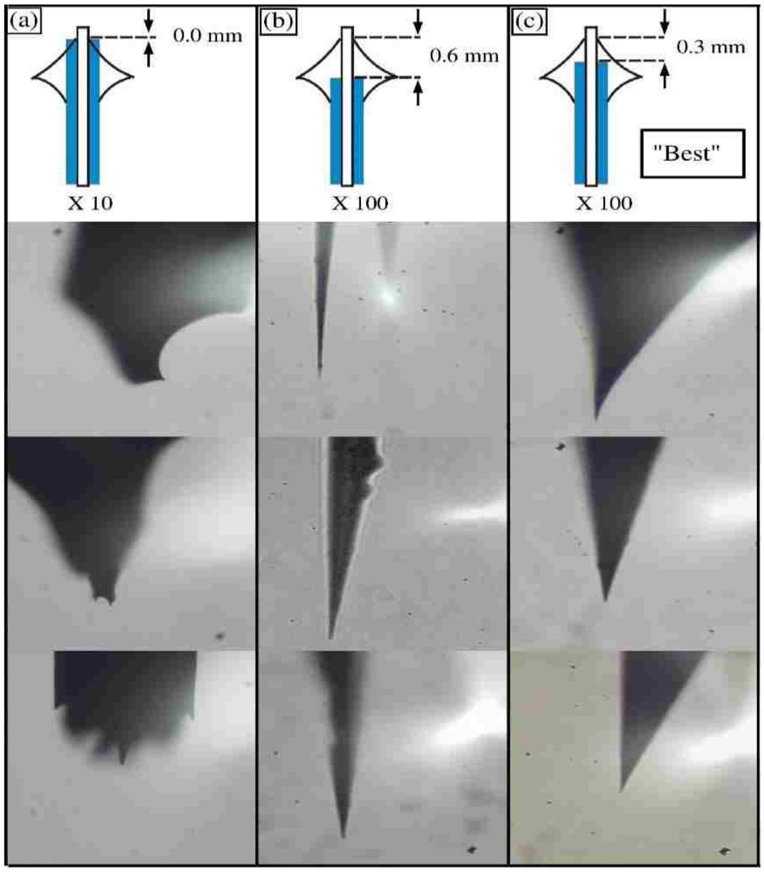

Figure 3.3 Optical microscope images of the particial etch stop tungsten (W) tips fabricated from a double lamella dropoff electrochemical etching method. The first row of this figure displays the schematic diagrams of each tungsten wire, the etch stop (blue color), etchant height from the etch stop and etchant levels. The numbers just below the schematic diagrams show the values of magnification of the etched tips displaced along the same column as the schematic diagrams. The first column shows optical microscope images at 10 x magnification of the three different W tips fabricated when the air/electrolyte meniscus level held by the upper gold ring was about 0.0 mm from the upper mark of the etch stop on the W wire during the etching process. At this level, all probes have non cone shapes. The second column represents randomely selected optimized optical images at 100x magnification of the W tips etched as the etchant height was about 0.6 mm. Here, most of all tips have sharp cone shapes. The third column illustrates the optical images at 100x magnification of typical electrochemically etched W tips immediately after dc etching and cleaning when setting etchant height at about 0.3 mm. Most of all etched tips have well controllable large cone angles. In general, etchant height plays an important role in determining the tips shapes.

The tungsten tip was fabricated when the initial air/electrolyte meniscus held by the upper gold ring during the etching process was about 0 mm in distance from the upper mark of the etch stop on the tungsten wire. At this level, we made more than 20 tips. After the fabrication of tips, the optical microscope was used to analyze the effect of etchant's height on the fabricated tip. Analysis of the etched tips using an optical microscope confirmed that 100 % of the etched tips had non cone shapes and difficulties finding their radii due to the non-conducting nature of the etch stop during the etching process. At this level, each tip was fabricated for an average period of 90 min. The first column of figure 3.3 indicates some of the randomely selected optical microscope images of three different etched tungsten tips at a magnification of 10 X. When looking at the results of the first column of figure 3.3(a), the optical images gave us a signal to identify the shapes of the tips. Clearly, all tips were non cone shapes. Some facts around these results were observed during the etching process. The first possible cause for these results was most likely that the etch stop could not freely etch the W wire because of interrupt the flow of current. Second, when the W wire was etched, the etch stop fell on the apex of the tip at the end of the etching process. These explanations were proposed by our research group.

In the next step, to optimize the cone angle of the etched tip and its aspect ratio, etchant height was increased to a level of 0.3 mm and then 20 tips were fabricated. After the electrochemical etching and cleaning, the tips' shapes were immediately evaluated by an optical microscope at the higher magnification: 100x. 80 % of the tips had bigger cone angles while 20% of the tips had smaller cone angles. The third column of Figure 3.3 indicates high-magnification optical microscope images of three different tips taken after the fabrication of tungsten wire during electrochemical etching. From these images, one could observe that all tips had nearly the same cone angle with smooth surface areas. The average etching time for a tip was measured to be 40 min. At 0.3 mm meniscus's level, the etch stop collapsed just below the tip at the end of the etching process. Similar observation were made observed during the fabrication of each tip.

Finally, to check the optimized results, we chose an etchant's level of about 0.6mm and then made 20 tips at room temperature. The quality of the etched W tips was characterized by an optical microscope at a magnification of 100x. When the inspection of the tip shapes under the optical microscope was done, we compared the tips' shapes to each other. In this study, 85% of the etched tips had the sharp cone shape whereas 15% of the etched tips had bigger cone shapes. Some of the most realiable reasons around these results have been already discussed in sections: 3.2 and 3.3 respectively. At this setting, the etch stop was far below the final etched tips. Some of the typical higher resolution optical images of etched tips are presented along the second column of figures 3.3. The apex of the tips in figure 3.3 (b) looks clean and sharp. The etching duration of the tip was about 30 min.

From the above discussion, we found that the varied etched tips shapes were mainly due to the position of etchant heights during etching. When the etchant height from the etch stop on the W wire was increased during the etching process, the shape of the tips was changed from non-cone to bigger cone and then bigger cone to sharp cone respectively. Thus, three kinds of tips shapes were possible: non cone shape, sharp cone shape and bigger cone shape at three different etchant heights of 0.0 mm, 0.3 mm and 0.6 mm from the upper mark of the etch stop on the W wire. With an optical microscope, it was easy to distinguish one of these possibilities from another. Comparing the shapes of the etched tips in Figures 3.3 (a),

(b) and (c) suggested that the cone angle and shape of the etched tips were varied due to the etch stop on the W wire which played a key role in controlling the tips shapes during etching. From figure 3.3, we could oberve that the bigger cone shaped tips were found when the etchant height was at 0.3 mm. Thus, we believe that we are able to control the shapes of the particial etch stop W tips at different etchant's level fabricated under a double lamellae dropoff electrochemical etching method.

CHAPTER FOUR

SUMMARY, CONCLUSIONS AND FUTURE RESEARCH APPROACH

4.1 Chapter overview

This chapter provides the summarized experimental results obtaining from chapter two. After summarizing the results, conclusions and a future research approach are presented below.

4.2 Summary and Conclusions

The commercially available tungsten tip is one of the metal tips used in spectroscopy measurements. To obtain the quality data in spectroscopy, a well-shaped tip with a low aspect ratio is required. This goal depends on which methods are used to etch the tips. In general, the main focus of this research was to understand the electrochemical etching process and then fabricate several tips from vertically-aligned tungsten wire using a custom designed three reliable electrochemical etching methods, each discussed in chapter 2: submerged method, single lamella drop-off method and double lamella drop-off method. All of these methods were demonstrated at room temperature in the Department of Physics, University of Arkansas Fayetteville and discussed the possibility of etched tips' shapes. These techniques were capable of producing well controllable tips' shapes. After etching, a chemical method to clean the etched tips was utilized. An optical microscope was used to analyze the etched tips surfaces. A summary of results obtained from etching methods is below:

In the first case, several vertically-aligned tungsten tips were etched via the submerged electrochemical etching method and then analyzed by optical microscope. The effect of biased potential applied between working electrode and counter electrode on the shape of the etched tip was investigated. As expected, the tip's shape was dramatically changed with the varied biased potential. This effect was observed in chapter 2 at four different potential levels: 3.5 V, 4.5 V, 5.5 V and 6.5 V with constant etching current, 4 mA. The results in chapter 3 showed that the etched tips' shapes were strongly affected via the biased voltages. First, the cone angle of the tip was increased along the direction of an increase in applied potential from 3.5 V to 4.5 V with an etching current 4 mA. Second, it was decreased in the opposite direction of the increase in applied potential from 4.5 V to 6.5 V with an etching current 4 mA. In general, the bigger cone shapes were observed at a biased potential of 4.5 V with etching current of 4 mA.

In the second type of electrochemical method, a single lamella drop off electrochemical etching method, several tungsten tips were fabricated with an electrolyte concentration as 8 gm of NaOH in 100 ml deionized water with a biased potential 4.5 V. Our results under a single lamella method demonstrated in chapter 3 suggest that similar tips which might be suitable for spectroscopy measurements could be produced at a biased potential of 4.5 V. In comparison with the results obtaining from submerged electrochemical etching method at a biased of potential 4.5 V, similar cone shape tips were also achieved by this method at a potential of 4.5 V.

Finally, the various aspects of etched tips have been investigated using a modified double lamella drop off method with the various levels of etchant's heights from the upper mark of the etch stop (nail polish) on the tungsten wire during etching. In general, the correlation of shape and aspect ratio of the tips with etchant height were systematically investigated in such a way that it was easy to point out the condition of the bigger cone angle etched tip. This was the first time that the shape of the vertically aligned tips was controlled via a double lamella method. It was inferred from optical images of the etched tips that the tips shapes primarily affected the etchant heights. With using an etch stop, we found that most all tips: none cone shape, bigger cone shape, and sharp cone shape tips were produced at etchant heights: 0.0 mm, 0.3 mm, and 0.6 mm respectively from the upper mark of the etch stop on the W wire. These results showed that the shapes and aspect ratio of the tips were found to vary with the etchant heights. Thus, we were able to control the tips shapes using a 0.05 mm thick film of etch stop coated on the surface of the W wire which was enough to result in three different kinds of tips shapes. Based on these results, we prefer to use tungsten tips fabricated at 0.3 mm ehchant height in spectroscopy measurements.

The three different techniques mentioned above used for the etching of tungsten wire can also be used to fabricate other types of metal elements such as Gold (Au), Platinum/Indium (Pt/In), Aluminum (Al) etc. Thus, these methods are beneficial to understand about the fabrication of varied tips from a range of metals.

4.3 Future research approach

Electrochemical etching of particial etch stop tungsten wire via a double lamella drop off method will continue for making larger cone angle tips. To test the quality of tips, they might be used in spectroscopy measurements. If tips have bigger cone angles with a low aspect ratio, they can play a key role in analyzing the sample at the atomic scale through spectroscopy measurements. Overall, the goal of these measurements is to analyze a new material in various aspects at its atomic level.

I hope this thesis will give a general idea regarding the metal tips' making process and may be interesting for researchers who use this process to etch the metal tips which might play an important role in taking the quality of scanning tunneling microscope (STM) images.

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