NRAO CHEMICAL LAB REPORT NO. 3

A CHARACTERIZATION STUDY OF POINTING METHODS FOR HALF-MIL PHOSPHOR BRONZE WIRE

A Thesis

In Humanities 402

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In Partial Fulfillment

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Bachelor of Science Chemical Engineering

by

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On my honor I pledge that this work is my own.

Received, agreed, 7 April
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ABSTRACT

Phosphor bronze wires were pointed from a 13- m diameter to a 2- m tip to contact a 2- m Schottky-barrier diode. The pointing was done by placing the wire as an anode in an electrochemical cell. The electrolyte used was 4 % sulfamic acid with glycerine added in variable quantities. The primary pointing mechanism is thought to be related to the fact that the solution meniscus lowers as the wire diameter decreases. Increased ambient air humidity produced wire points that were too sharp (0.5 - m). The wire insertion depth was noted to be an independent variable affecting the point shape. Small depths caused short cones and large depths caused long cones. Procedure are detailed for a 50 % to 80 % yield of usable points for diode contact.

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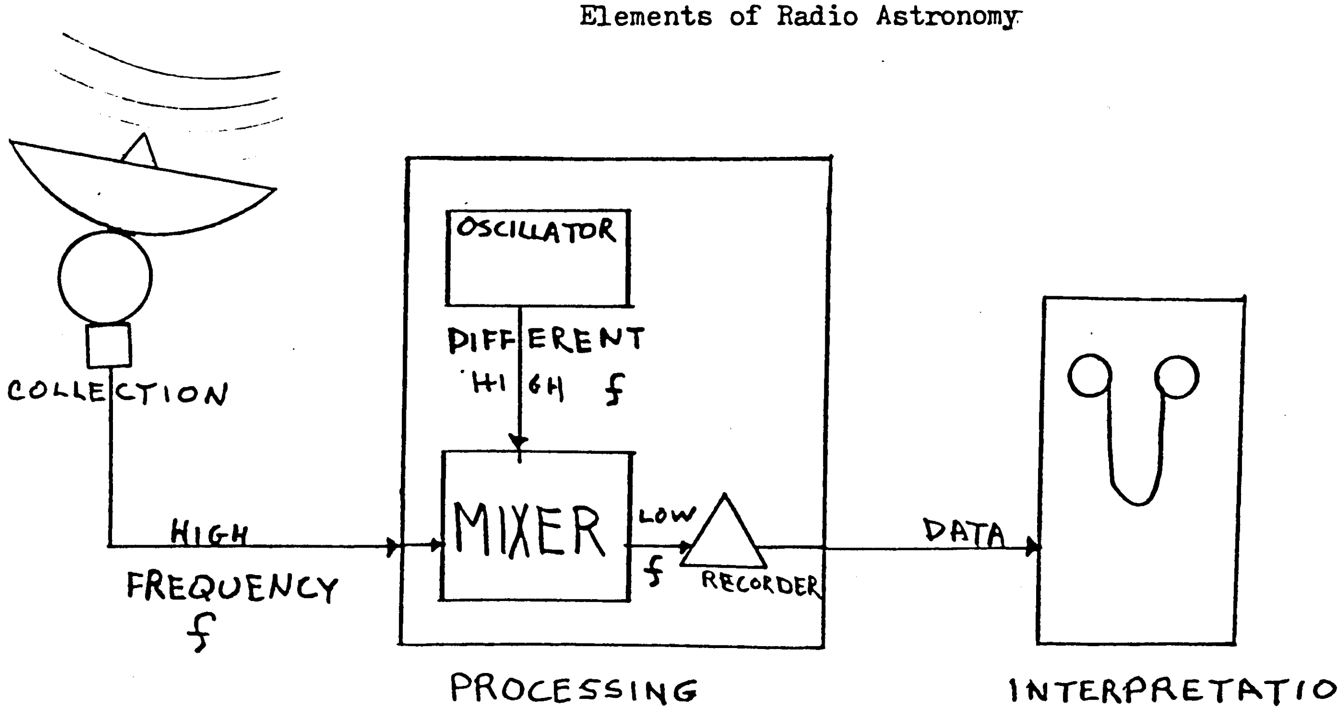
INTRODUCTION

This project is a study to characterize the process of sharpening small wires (whiskers) of phosphor bronze to a point that will contact a Schottky-barrier diode. The wires are 13-micrometer diameter phosphor bronze and the diodes are 2-micrometer round dots of platinum on gallium arsenide. The whiskers sharpened during the project were to be used by the National Radio Astronomy Observatory (NRAO), which funded the project. Results from the study will help formulate an optimum procedure to sharpen whiskers.

Background

Radio astronomy has three major elements, signal collection, signal processing, and signal interpretation (Figure 1). Dish-shaped antennas collect the signal, which is usually between 20 and

Figure 1
Elements of Radio Astronomy



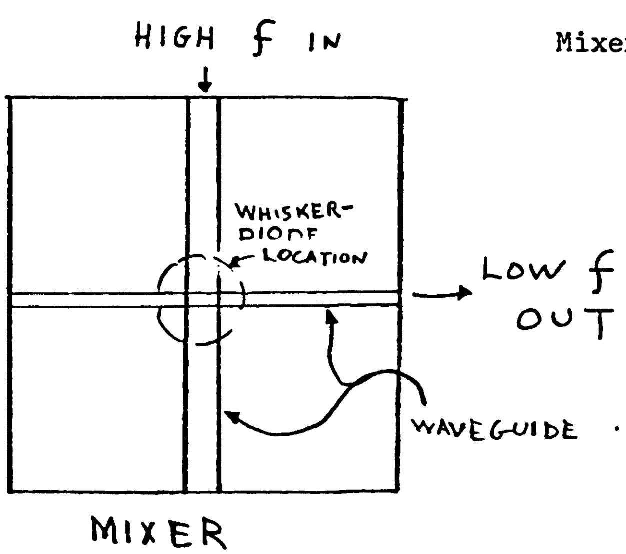
300 gigahertz (10^9 hertz). This high frequency is combined in a mixer with another slightly different high frequency from a local oscillator. When two frequencies are mixed together both the sum and the difference are available. The mixer is designed to propagate only the low-frequency difference, which is then recorded. The recorded data are given to astronomers, who interpret its meaning.

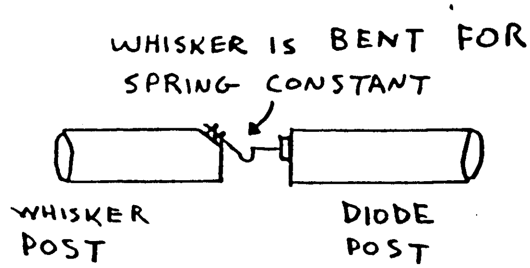
Typically in radio astronomy the radio signal is about three orders of magnitude smaller than background noise. This background noise consists of ambient noise and internal noise. Ambient noise is generated mainly by the electrical and electronic devices used in our technological society. Electronic systems also generate internal thermal noise. Mixers are operated at cryogenic temperatures (10K-20K), to alleviate the thermal noise problem.

The Whisker-Diode Contact

The whisker-diode contact is the main component of the mixer used to reduce the gathered frequency, (Figure 2). Through this contact the local oscillator signal is directed. Much research

Figure 2
Mixer Arrangement



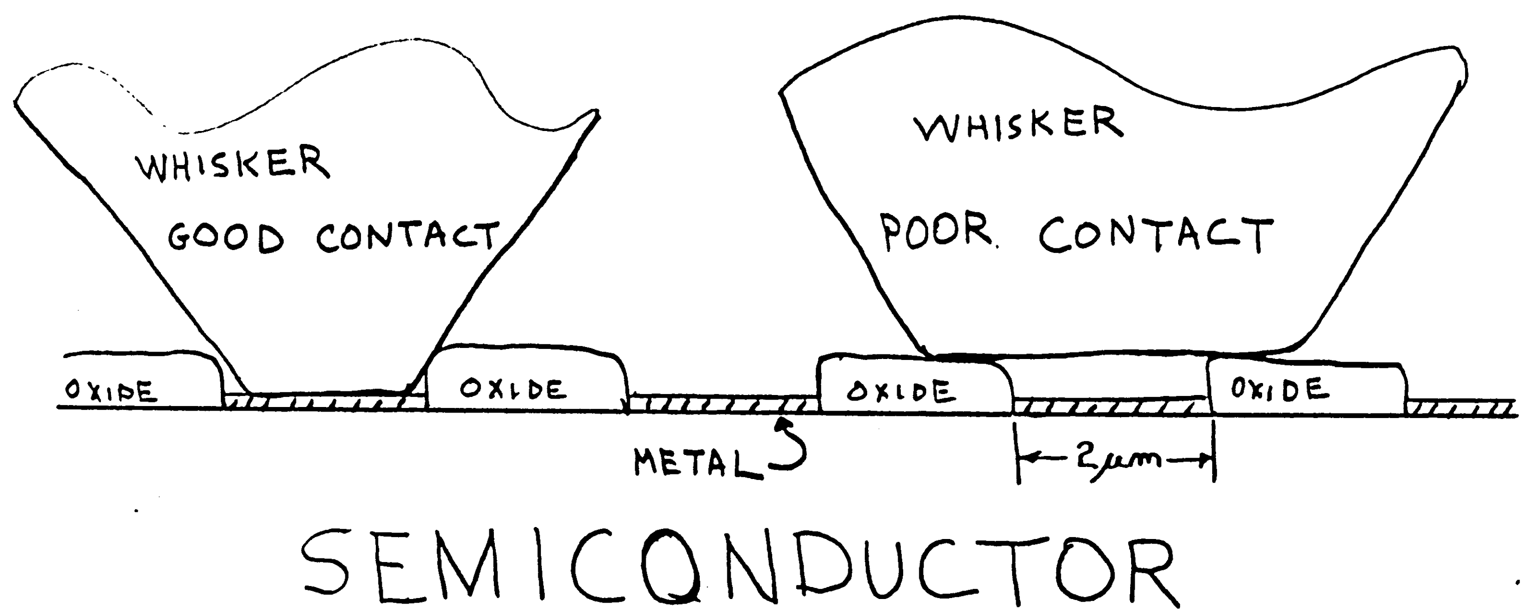


has been done on the electronics of mixers, and various mixer designs are used. The operating frequency determines the specific design needed. Development of more efficient mixers continues to lower the thermal noise contributed by the mixing device.

One component in the mixer that contributes noise is the diode. Currently, Schottky-barrier diodes are used for their very low-noise property. Schottky-barrier diodes consist of a semiconductor which has been coated with a metal. The semiconductor-metal interface acts as the rectifying junction.

The Semiconductor Device Laboratory at the University of Virginia presently fabricates the lowest-noise diodes available. This lab, instituted by Dr. Robert Mattauch, provides NRAO with diodes which use a platinum-gallium arsenide interface. The platinum is in the form of 2-micrometer dots arranged in a square matrix with centers that are 4-micrometers apart. This arrangement gives a very high density of diodes. There can be as many as 15000 diodes, (of which only one is used), on a single 0.26-mm^2 chip. Contact must be made with the metal on one of these diodes. The whisker's point must measure less than 2 microns across for a good ohmic contact with the diode, (Figure 3). The 2-micron point insures that the whisker will touch the metal and not the diode-defining oxide.

Figure 3
Whisker-diode contact



THEORETICAL CONSIDERATIONS

Electrode Process

The pointing is done in an electrochemical cell where the whisker forms one of the electrodes.

> When a metal is immersed in a solution of its ions, an interaction occurs between the metal and solution such that the metal sends ions into the solution, whilst, conversely, the solution deposits ions on the metal, which are incorporated into the metal lattice.[1]

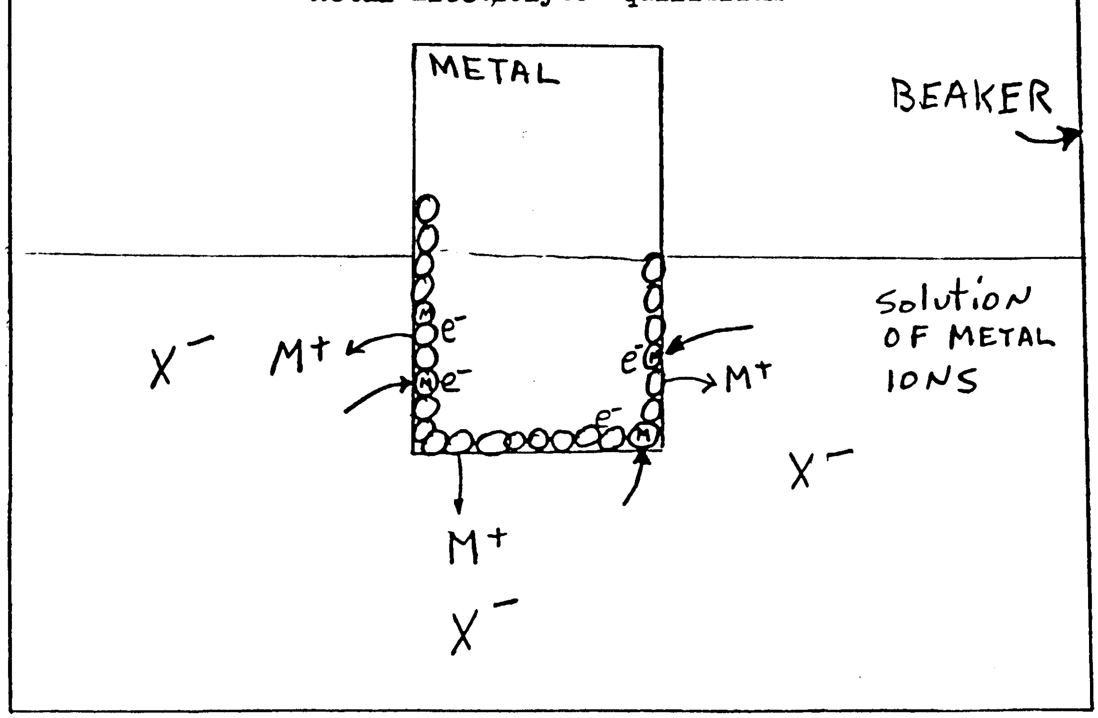
This equilibrium, pictured in Figure 4, can be generally represented by the following equation.

$$X^{-} + M = M^{+N} + Ne^{-} + X^{-} \qquad (1)$$

Where M is the metal, M^{+N} is the metal ion, N is the valence charge and the number of electrons (e^{-}) liberated. N is often 1 or 2. X^{-} is a spectator ion which does little in the reaction but is needed for overall solution neutrality.

Figure 4

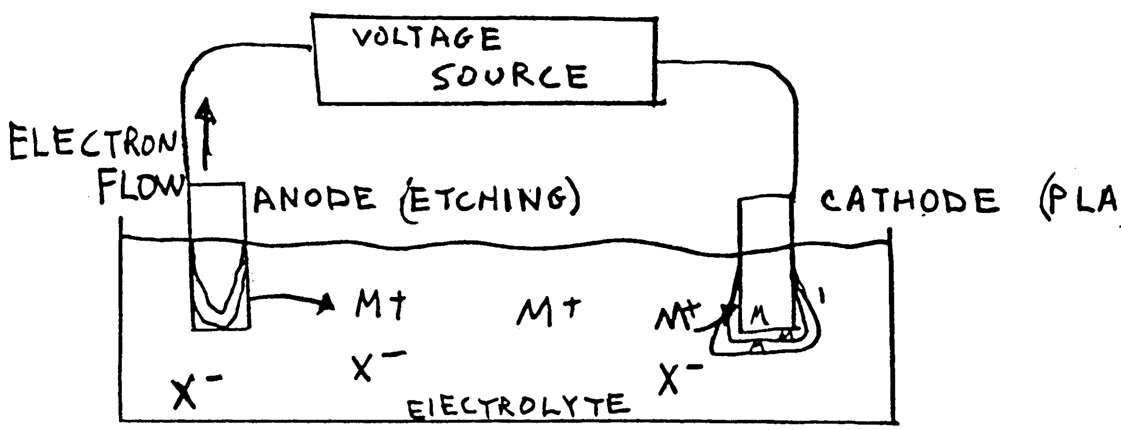
Metal-Electrolyte Equilibrium



A voltage applied to the metal can shift the equilibrium toward metal ion deposition (electroplating) or toward metal dissolution (etching) depending on the polarity of the voltage. In an electrochemical cell, electrodes are placed in an electrolyte, (current conducting solution), and wired together with a voltage source in series (Figure 5). Metal ions dissolve from the anode and deposit on the cathode.

Figure 5

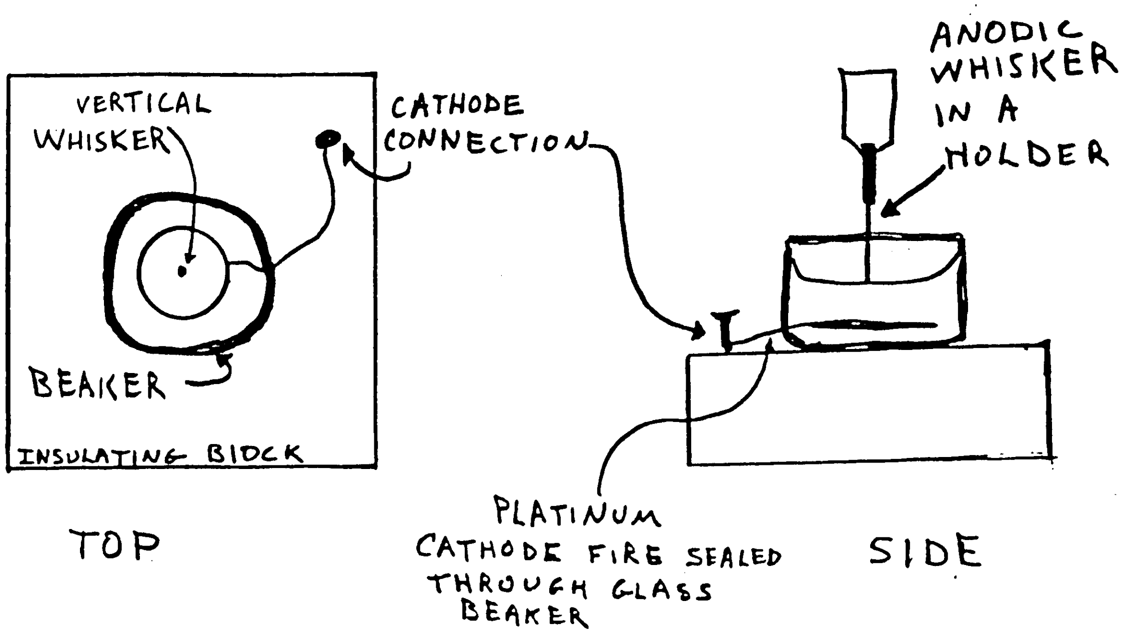
General Electrochemical Cell



In the above arrangement, etching and plating occur over the total surface of the immersed electrode, but they are uneven. Plating and etching occur at a higher rate on the areas where the distance between electrodes is small. This causes the sides of the electrodes facing each other to etch or plate more rapidly. The uneven etching in such a cell would be unacceptable for the production of smooth conical points. Therefore, when etching points, the anode-cathode placement is as shown in Figure 6.

Figure 6

Whisker-Etching Cell



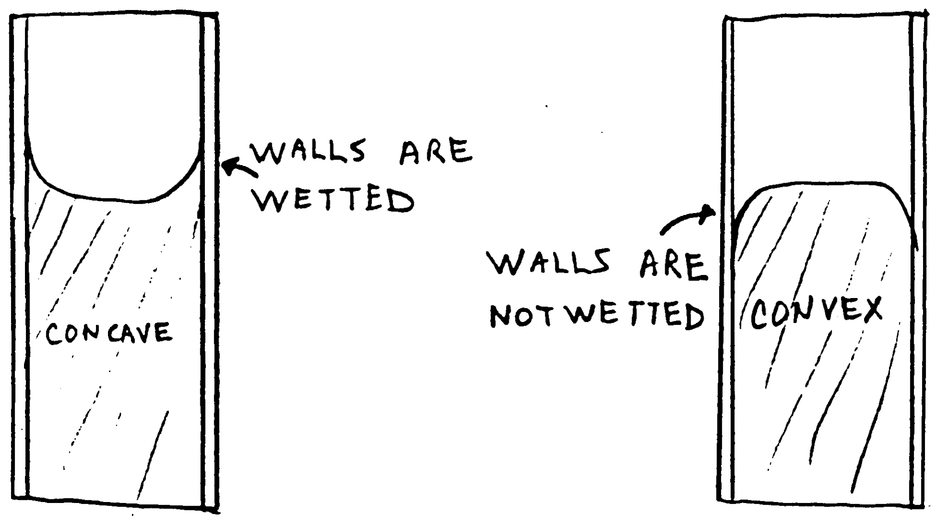
A platinum cathode is in the form of a ring on the bottom of the beaker. Etching is more uniform when the wire to be pointed is placed in the center of the ring and at the top of the solution. as the anode-cathode distance is essentially equivalent 360 degrees around the wire.

Meniscus Effect

When a whisker is in contact with the solution, there is a meniscus effect. A meniscus is the curved upper portion of a body of liquid in a column (figure 7). The meniscus can be concave if the walls of the container are wetted by the liquid and convex if the walls are not wetted.

Figure 7

Menisci in a Vertical Tube

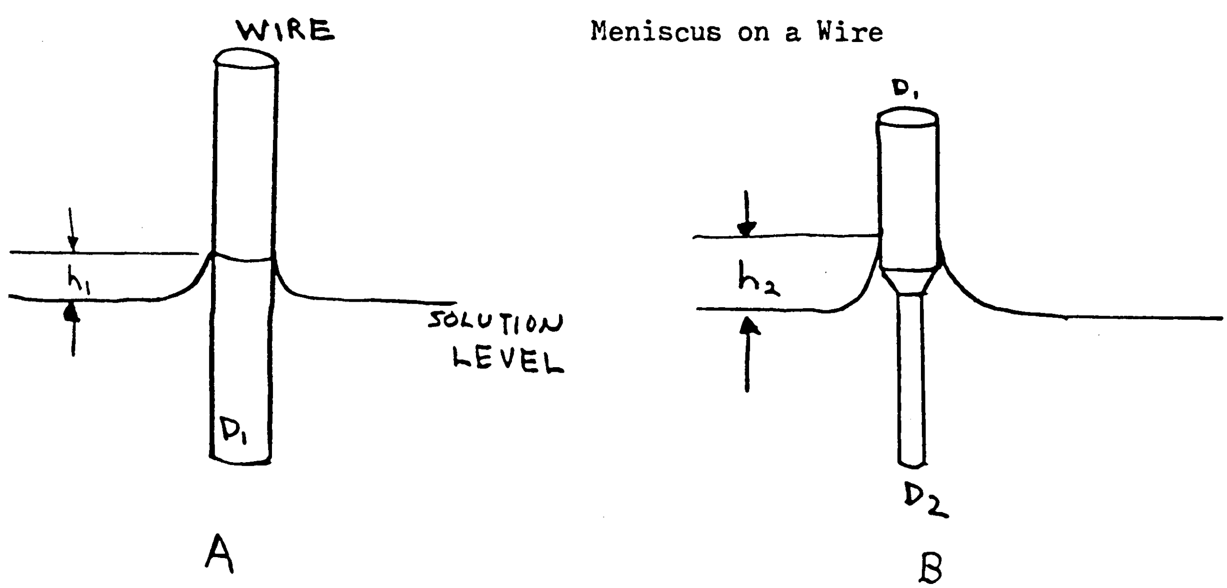


A meniscus will exist on the outside of an immersed object as well as the inside.

Clean phosphor bronze is wetted by aqueous solutions and the meniscus rises to a height h_1 as shown in Figure 8A

Figure 8

Meniscus on a Wire



The height, h, if inside a cylinder, is a function of three parameters. The parameters are the wire diameter, D, the liquid density, and the surface tension of the solution, $T(\rho)$. The surface tension is a function of the difference in density of the liquid and vapor above the liquid. These two relationships are Equations 2 and 3.

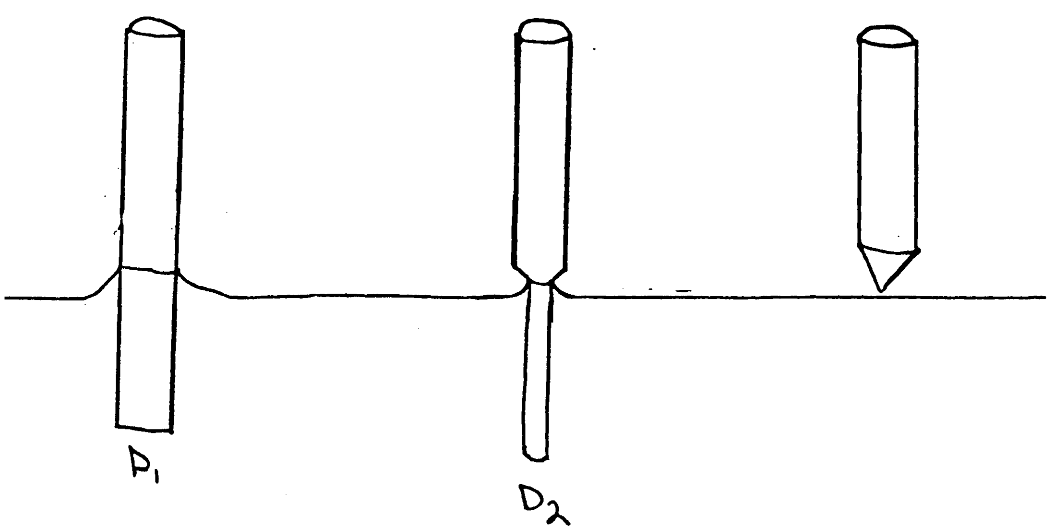
$$T(\rho) \propto (\rho_L - \rho_g)^4 \quad \text{REF. 2} \qquad (2)$$

$$h = \frac{4T(\rho)}{D\rho\left(\begin{array}{c}\text{gravitation} \\ \text{constant}\end{array}\right)} \quad \text{REF. 3} \qquad (3)$$

Equation 3 indicates that the height rises as the diameter decreases. On the perimeter of a wire which is being etched, an increased meniscus height seems unlikely (Figure 8B). In fact, the height of the meniscus viewed through a microscope during the etching process decreases until the whisker is pointed (Figure 9).

Figure 9

Falling Meniscus During Etch



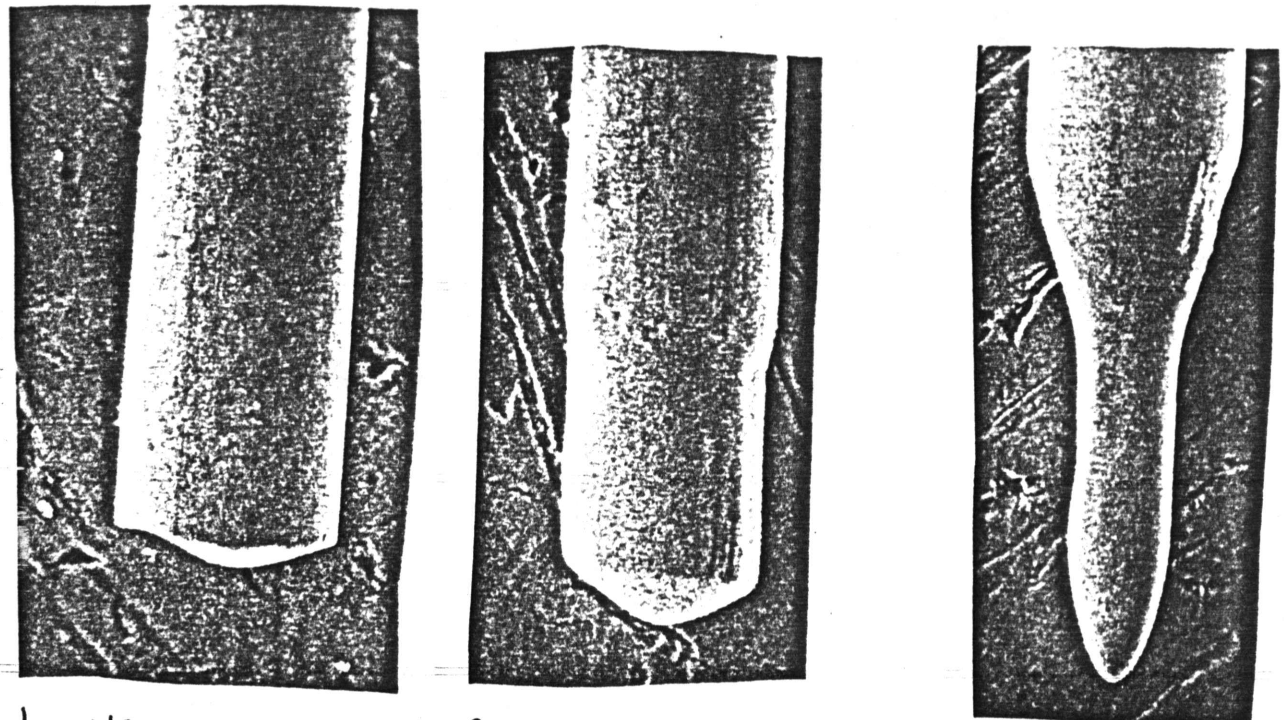
The decreasing height suggests that the height is directly proportional to the diameter.

The driving force available to lift the solution on the wire is supplied by the surface tension and the physical line on which the driving force acts (in this case the circumference, πD).

$$\text{driving force} = \pi D T(\rho) \qquad 4$$

The force available decreases as the diameter decreases. Once the whisker is inserted into the solution, the meniscus height increases until the driving force is in equilibrium with an opposing force. The large-diameter portion of the wire acts as a physical barrier to the meniscus. The diameter decreases as etching proceeds and the meniscus force decreases, hence the height is decreased and the cone is formed.

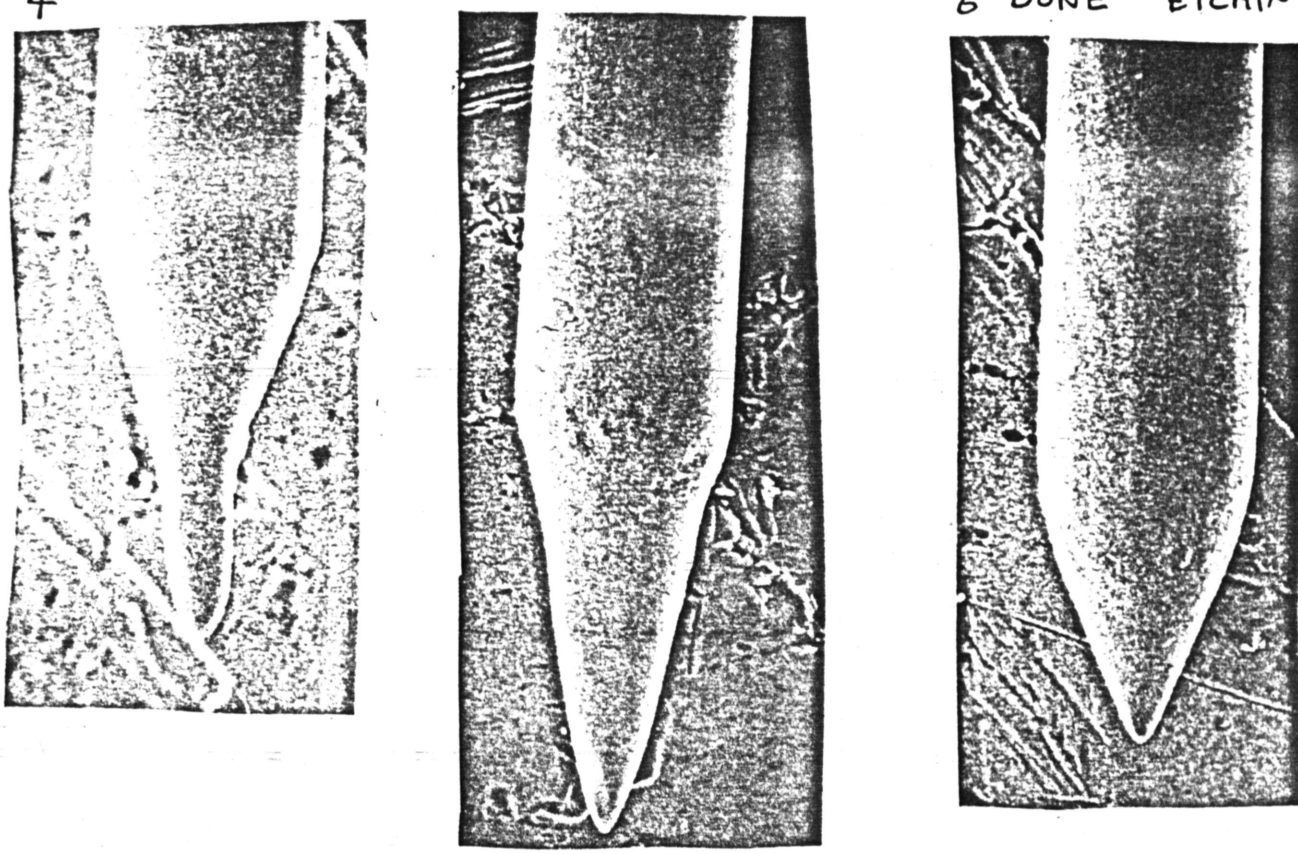
Photographs taken on a scanning electron microscope (SEM) give evidence of the decreasing height (Figure 10), which I believe to be the primary mechanism of the pointing. The SEM pictures are of different phosphor bronze whiskers during subsequent stages of the etching process. The upper left corner whisker has not been etched and the lower right corner whisker is finished.



1 NOT ETCHED 2 3

FIGURE 10
SEM PHOTOGRAPHS OF PARTIALLY ETCHED WHISKERS AT 2220 MAGNIFICATION

4 5 6 DONE ETCHING



EXPERIMENTAL WORK

Beginnings

The electrochemical pointing of 13-micrometer whiskers has in the past been a frustrating operation. At times, the yield of usable whiskers was as low as 10 percent, while on some days the yield approached 100 percent. A sequence of etching steps had to be established which would yield usable points about 50 percent of the time.

The existing skeleton procedure consisted of three basic steps.

1. Lower the whisker until it makes contact with the solution.
2. Etch the point with an applied voltage of 1.8 volts.
3. Rinse with water and inspect.

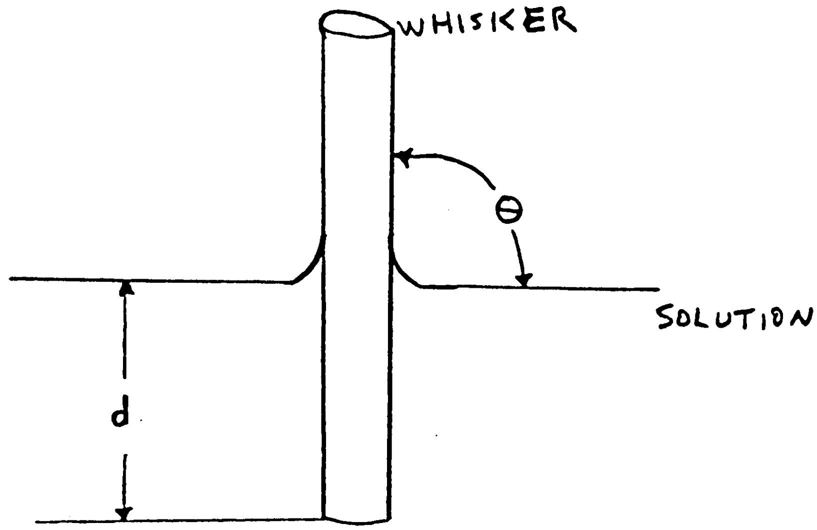
On days when the yield was good these instructions were adequate. The whisker ends would all be similar in shape and point diameter. On days when yield was low (usually very humid days) there was tremendous variation in both shape and point diameter. On such days the wire might not even have a point after the etch. A much more detailed procedure was needed.

Whisker-Solution Contact

The first thing that needed control was the whisker-solution contact. There are two parameters for that contact - depth of insertion, d, and contact angle, θ, defined in figure 11.

Figure 11

Whisker-solution Contact

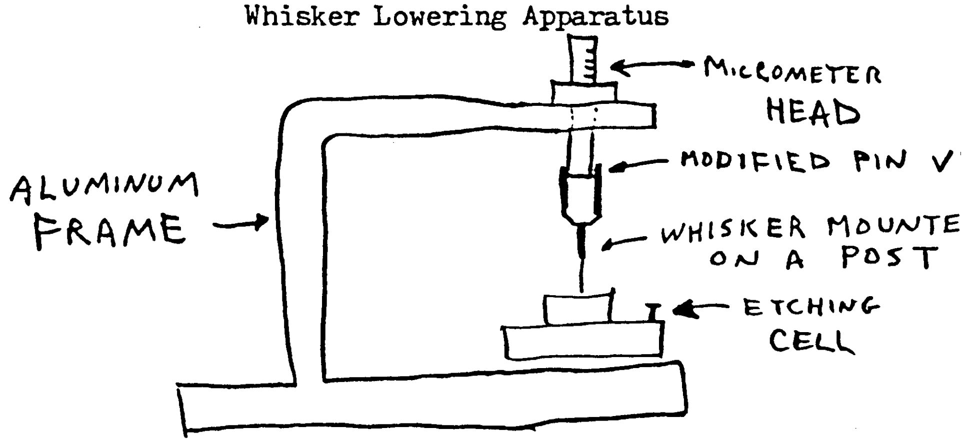


The depth of insertion needed to be repeatable, and the contact angle θ should be as close to 90 degrees as possible to avoid asymmetrical cones.

To assure repeatability of these two parameters the device in Figure 12 was designed and built by Mr. Gordon Green.

Figure 12

Whisker Lowering Apparatus



The micrometer head is a Starrett 55946 number 262RL non-rotating type. It is graduated in mils (0.001 inch), and is accurate to ± 0.0002 inches. The pin vise is a superior swivel head pin vise # 48-120. The handle has been removed with a hacksaw, leaving a hollow cylinder which will mount snugly over the movement of the micrometer head. The pin vise is used to hold a 0.020 inch nickel post which has the phosphor bronze wire butt-soldered to it. The wire is straightened with tweezers after the post is placed in the pin vise to insure a good contact angle. The micrometer insures precise whisker lowering.

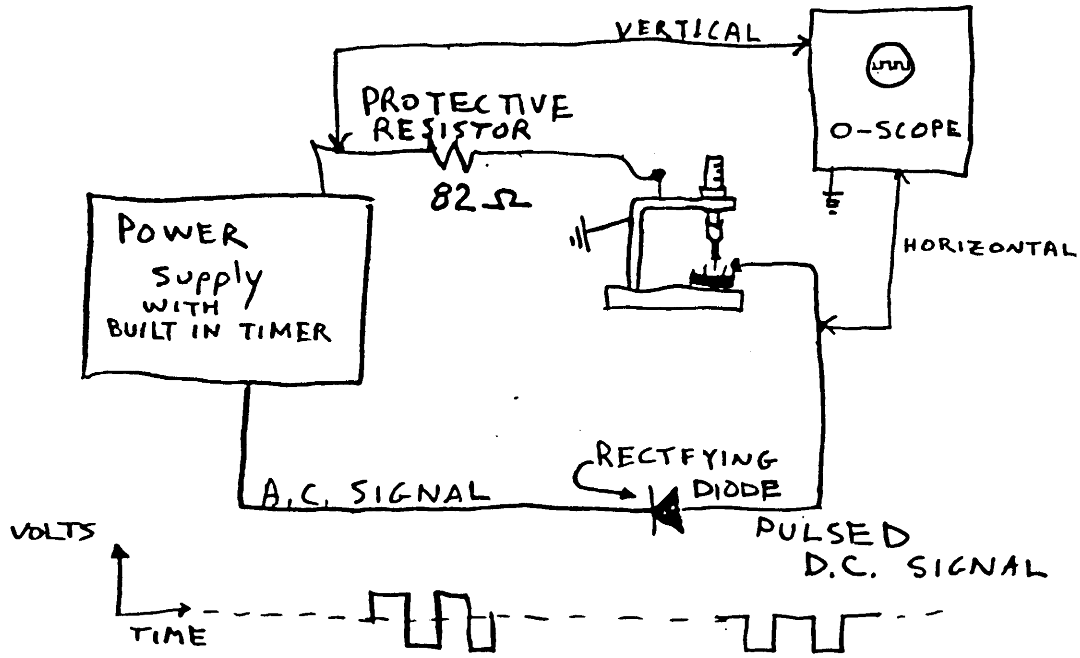
Etching Apparatus

The next thing that needed controlling was the etching current. The requirements were that the current should be instituted and terminated with precise, repeatable time intervals. I also felt that different waveforms might etch different-shaped points. Further, pulsed current was desired. During the time between pulses the metal and metal ions reach an equilibrium and during the short etching period the system is never very far from an equilibrium state.

One way to achieve short direct current pulses is to rectify an alternating current before it reaches the load (here the etching ce Figure 13 gives the circuit used during the project.

Figure 13

Circuit Used to Point Whiskers



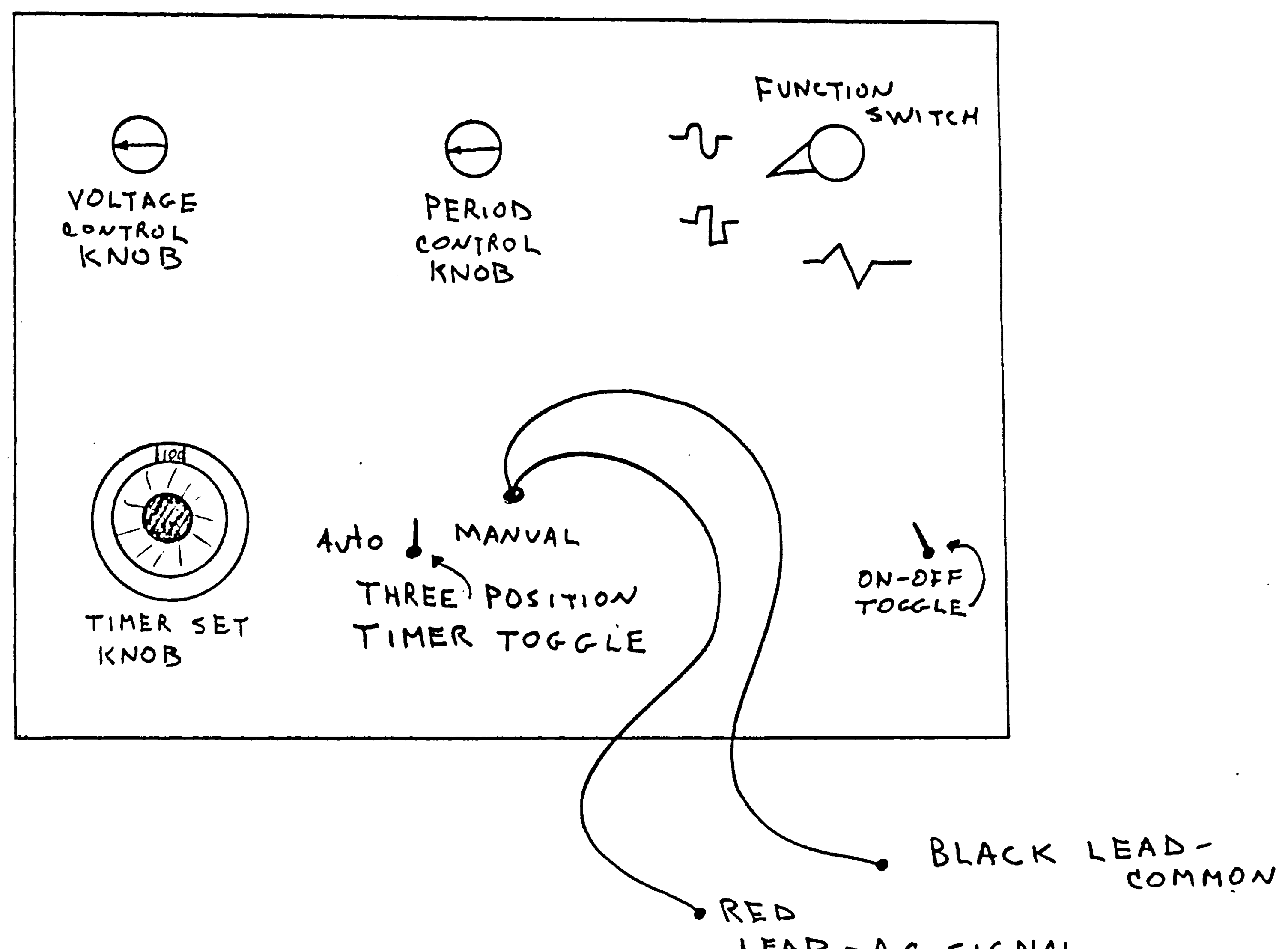
Mr. Gary Barrel, an electrical engineer at NRAO, designed and constructed an AC power supply which supplied full wave, square, triangular and sine waves (Appendix I gives a schematic).

The voltage and period of the signal were controllable and a built-in timer allowed repeatable etch times. A rectifying diode was placed in series with the etching cell to allow current to pass only in the direction which made the whisker anodic.

A solution of 4 percent sulfamic acid (NH_2SO_3H) was used at ambient temperature and pressure. The voltage across the 82-ohm resistor was set at 1.8 volts and the period of the pulses was 12.5 milliseconds with a 50% duty cycle. Wire length was about 1 cm. before it was etched, using the square wave function on the power supply. Variables for the pointing process were insertion depth and etch time.

FIGURE 14

DETAIL OF POWER SUPPLY



A comment should be made about handling half-mil phosphor bronze wire. This wire is extremely small and barely visible to the unaided eye. This wire is very easy to misplace, drop, or bend and difficult to pick up with tweezers. Each wire was therefore individually butt-soldered to the end of a thirty-mil nickel post which facilitated handling. A detailed procedure for soldering these wires while observing them under a microscope appears as Procedure I in Appendix I.

Phase I

The procedure used during phase I was developed for its repeatability. I thought if the following sequence of steps was followed precisely, the usable whisker yield would be higher.

Procedure II

This procedure assumes that the system has been assembled as described in Figure 13, with the voltage across the 82-ohm resistor set at 1.8 volts with a period of 12.5 milliseconds.

1. Secure the whisker post in the pin vise and straighten the wire with tweezers.
2. Place the pin vise on the micrometer movement.
3. Lower the whisker until it just touches the solution.
4. Etch the whisker, using the manual mode on power supply, until no more current will pass (less than 0.001^{V} on the o-
5. Lower the whisker 2 mils.
6. Set the timer. (Typical settings were 35% to 45% of full scale time or 400 to 550 milliseconds.)
7. Etch the whisker using the timer by pressing the toggle to the auto position (see Figure 14).

8. Remove the whisker; clean it in deionized water; and blow it dry with nitrogen.

9. Check the point for size and shape under a microscope.

Following this procedure had the immediate result of increased repeatability, but the whiskers were often too sharp on some days. These days seemed more humid and presumably the ambient air humidity was affecting the speed of the decreasing meniscus height.

It is clear from Equation 2

$$T(\rho) \propto (\rho_{liquid} - \rho_{gas})^4 \qquad 2$$

that small variations in the density of the gas would have a profound effect on the surface tension and thus the force available to raise the meniscus. To counteract this increase in gas density, glycerine was added to the solution, thus increasing the solution's density. Several (3 or 4) drops of glycerine were added to the beaker, which held approximately 3 milliliters of etching solution. The yield of good whiskers increased from about 30 % to about 80 %. solutions of 5%, 10%, 20%, 30% and 40% glycerine by volume were mixed and used during humid periods. A mixture of 10% glycerine was found to work well on days when the ambient temperature was around 75 F and the relative humidity was close to 40%. These two values represent a normal temperature and the highest humidity observed during the experimental period.

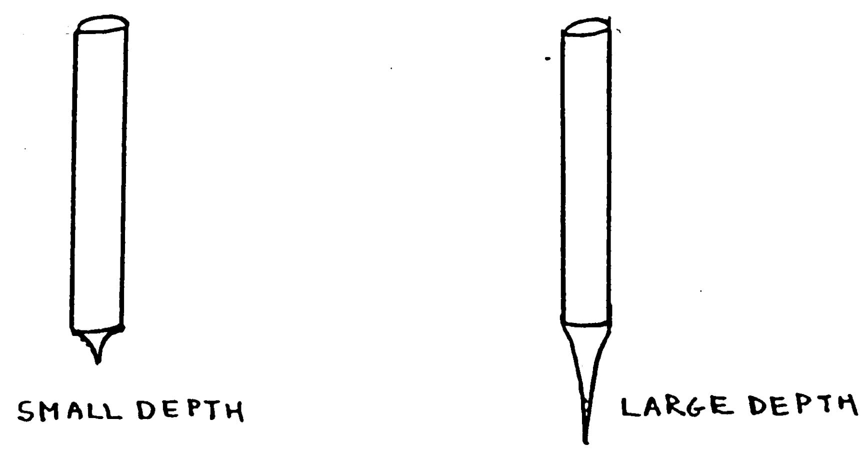
The shelf life of these solutions was about one month, after which the solutions began to smell of vinegar and would not produce sharp enough points.

Phase II

During the latter portion of the study, an effect was recognized that I had overlooked during Phase I. The procedure used in Phase I etched the whisker until no current passed (Step 4, Procedure II). The shape of the whisker point after this step was related to the initial insertion depth d (Figure 14).

Figure 14

Insertion Depth Effect



For the same meniscus height, the whisker points were short and extremely sharp for small depth, and long but again extremely sharp when a large depth was used.

The shape of the point after Step 4 in Procedure II had an effect on the final whisker point attained. The problem was that small variations in insertion depth had a large effect on the whisker point. The precise effect was erratic and has yet to be determined. The observa was used to increase the yield of satisfactory whisker points. The whisker was lowered 6 mils after it had just made contact with the solution. The percent experimental error in lowering the whisker

6 mils was much lower than that for the whisker just touching the solution, thus a uniform starting point for subsequent etching was the result. Procedure III is a result of this observation.

Procedure III

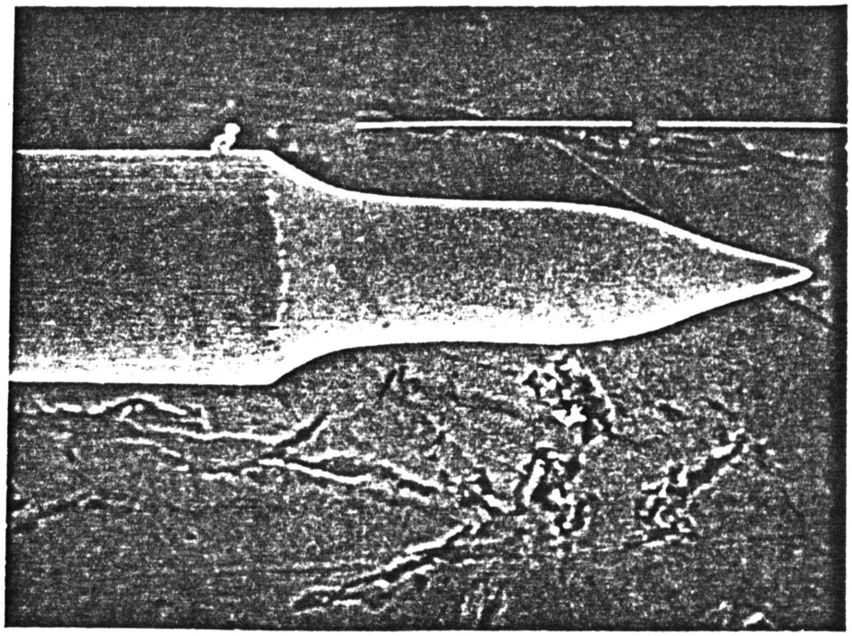
Again the apparatus is assembled and adjusted as in Procedure II.

1. Secure the whisker post in the pin vise and straighten the wire with tweezers.
2. Place the pin vise on the micrometer movement.
3. Lower the whisker until it just touches the solution.
4. Lower the whisker 6 mils.
5. Etch the whisker, using the manual mode on the power supply, for 30 seconds.
6. Lower the whisker 3 mils.
7. Etch the whisker twice, using the timer between 70% and 90% of the full-scale time value or a total of 1600 to 2000 milliseconds.
8. Lower the whisker 1 mil.
9. Etch the whisker using timer between 70% and 90% of the full-scale time value.
10. Remove the whisker; rinse it in deionized water; and blow it dry with nitrogen.
11. Check the point under a microscope.

A sample whisker made by using Procedure III is seen in Figure 15. The double cone found on the whisker in Figure 15 is a result of steps 7, 8 and 9 in Procedure III. Here the whisker is incompletel etched, lowered and etched again, thus forming a dual cone and a point diameter between 1 and 2 microns.

Figure 16

Procedure III Whisker



2600 MAGNIFICATION

The yield of usable whisker points from procedure III ranged fro[m] 50 % to 80 %.

Summary

The primary mechanism, meniscus effect, caused a point to form on the wire. A power supply was used which delivered timed amounts of square-wave alternating current. The square wave was rectified, giving the effect of pulsed direct current in the electrochemical etching cell, with the whisker as the anode. Very short current pulses with a period of 12.5 milliseconds allowed control of the lowering the meniscus height and the pointing of the whisker.

Procedure II was developed to control the insertion depth and contac angle of the whisker. A ten percent glycerine in sulfamic acid solution was used on days when the humidity reached close to 40 percent. An insertion depth effect was recognized and Procedure III was used to allow for the depth effect. A second timed etch was added to Procedure III which gave rise to the dual cone.

Conclusions

Both procedures used during this study can be used to etch satisfactory whisker points. Procedure II is limited to use during low humidity days (10% - 20%). Procedure III can be used during low humidity days or when the humidity reaches 35% to 40%. Whisker pointing was not attempted on days in other humidity ranges. Evidence for the exact depth effect was not gathered, but the effect was circumvented by lowering the whisker enough that small variations in depth did not affect the etched point. The third etching sequence included in Procedure III gave a dual cone and a satisfactory point. If this second cone was not desired, the duration of the second etch could be increased to complete the etching of the point, and the third etch could be omitted.

Recommendations

Procedure II consistently gave the highest yield (50 - 80%) of satisfactory whisker points. Further study is needed on the relatio of humidity to the percent glycerine required to adjust the solution density. A possible secondary pointing mechanism, recognized in Phase II as the depth effect, should also be characterized. Finally, the electrical properties of the dual cone whisker points should be examined.

REFERENCES

[1]Raub, E. and K. Muller, Fundamentals of Metal Deposition. Elsevier Publishing Company, New York, 1967, page 30.

[2]Perry, R. H., and Cecil Chilton, editor, Chemical Engineers' Handbook, Fifth Edition, McGraw-Hill Book Company, New York, 1973, pages 3 - 240.

[3]Weast, R. C., editor, Handbook of Chemistry of Physics, Fifty-Sixth Edition, Chemical Rubber Publishing Company, New York, 1975, pages F - 111.

APPENDIX I

Procedure I

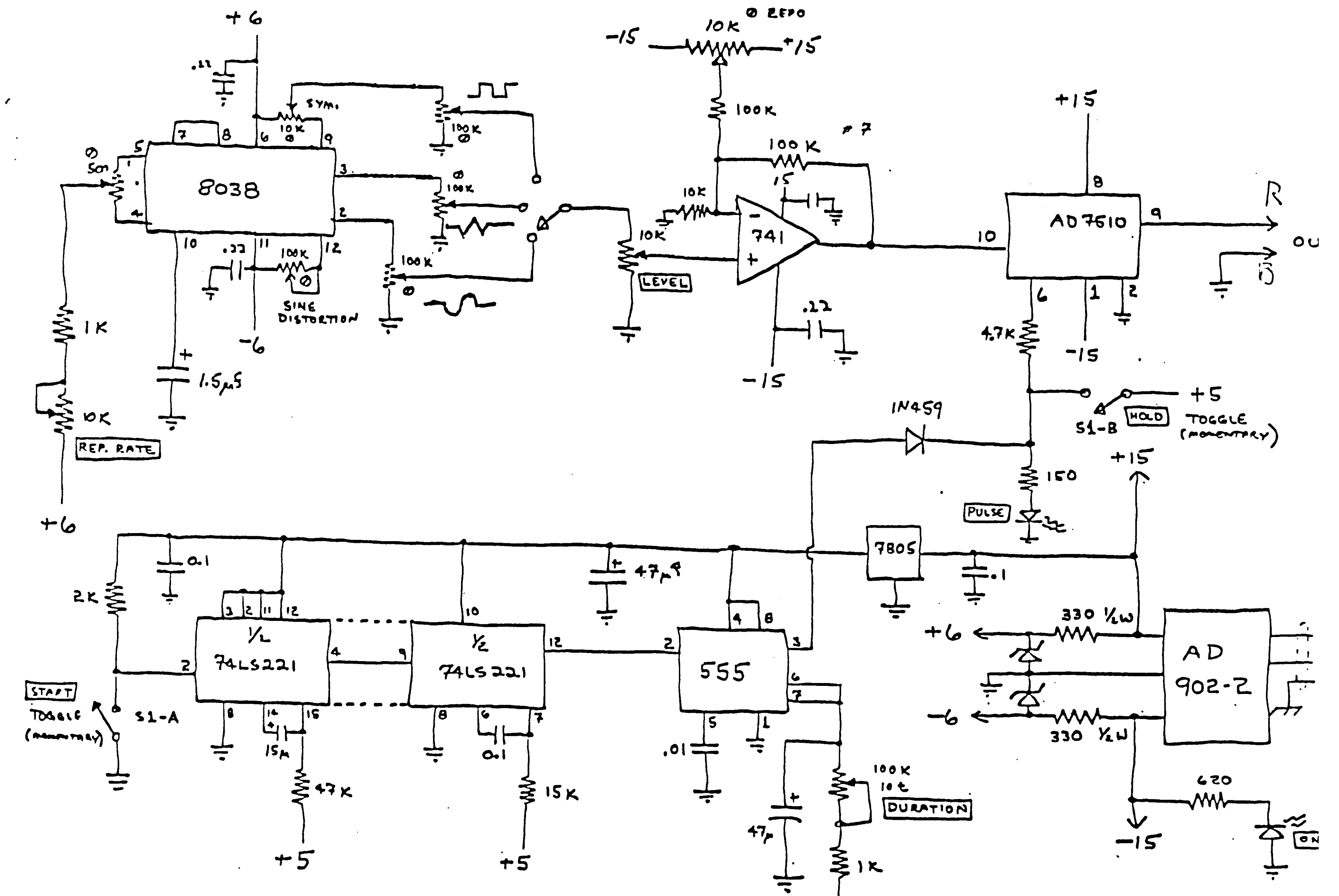
Whisker Handling Prior to Etching

1. Cut about a dozen pieces of $\frac{1}{2}$-mil phosphor bronze (grade C) wire 0.5 inch long.
2. Using #5 fine-point tweezers, secure one piece of wire in a tweezer holder which has an x-y-z positioning stage.
3. Place a nickel post in a free standing pin vise and secure it - position the vise under microscope.
4. Using a Variac soldering tweezers, melt a dot of TIX solder on the end of the post. (Use TIX flux.)
5. Position the wire in contact with the dot of solder and heat to solder in place with the Variac soldering tweezers.
6. Release the whisker; remove post from pin vise.
7. Clean in methanol with ultrasonic agitation for 5 seconds.
8. Place in a box until each wire in the batch is soldered.
9. Repeat steps 2 through 8 until batch is soldered.
10. Clean each whisker as follows:
    a. Place in hot alconox solution with ultrasonic agitation for 25 seconds.
    b. Rinse in hot tap water.
    c. Rinse in deionized water.
    d. Blow dry with nitrogen.
11. Place in box until ready to etch.*

*Note if over 2 days passes before etching is done,repeat Step 10.

APPENDIX II

On the following page is a schematic of a power supply which when used will produce continuous pulses or a timed period of pulses It produces a small current (20 mA) which is enough to etch points on whiskers.



CIRCUIT FOR POWER SUPPLY

GKB