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Very Sharp Platinum Tips by Electrochemical Etching

Bachelor Thesis

For obtaining the academic degree
Bachelor of Science

Bachelor Program of Technical Physics

Graz University of Technology

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Graz, May 6, 2012

Contents

1 Introduction

The tips used up to now to make electrical measurements in an SEM at the SEM laboratory of the Institute of Solid State Physics [1], are industrially manufactured tungsten tips (see Fig.1.1). To make electrical contact, the tip has to be pressed very hard on the surface of the sample and because the tip is very sharp (about 500 nm) it bends. So the contact between the tip and the sample is not at the head of the tip, but somewhere behind. It is also not possible to say how big the contacting part of the tip is. So the aim of this project was to try and make very sharp Pt/Ir tips, test their elastic and electrical properties and test if these tips are more suitable for the electrical measurements which are currently done at the SEM laboratory. The project is based upon the paper *Very sharp platinum tips for scanning tunneling microscopy* [2].

The produced tips have a sharp shape and are about 60 - 150 nm thick at the end. (See Figs.3.8 and 3.10) They also have good electrical properties, if the oxide layer is being removed. It there is an oxide layer, however, there is then a problem in making contact with the sample. During the project it was not possible to make good contact between a Pt/It tip and the silicon samples which were analyzed at the time, but there was good contact between the tips. The resistivity was about 30 - 50 Ω.

The elastic properties were not as bad as expected, but nor were they as good as hoped. After crashing on the surface the tip went back a bit, but it was bent (see Fig.3.7).

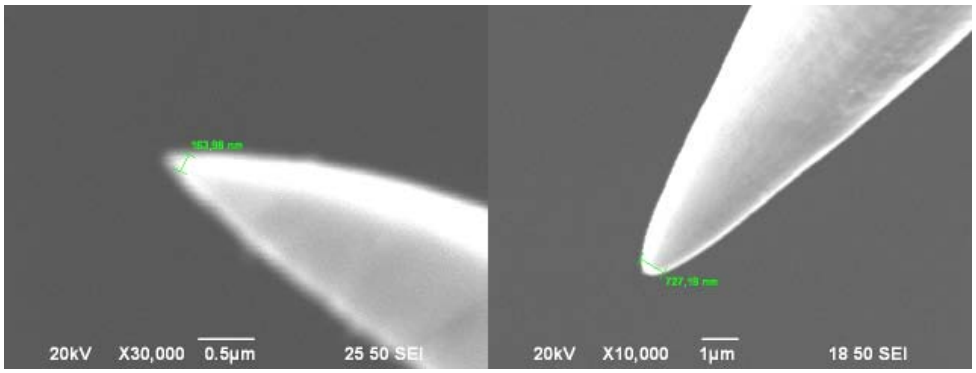
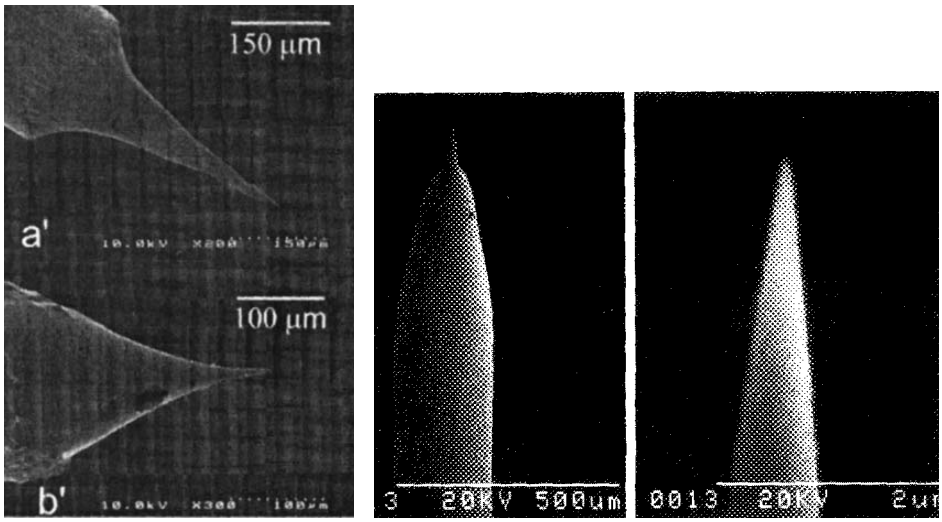


Figure 1.1: An etched Pt/Ir tip (left picture), compared with an industrially manufactured tungsten tip (right picture)

2 State of the art

2.1 Electrochemical etching

The electrochemical etching of very sharp tips is an established procedure for scanning tunneling microscopy [5]. It is possible to make tips out of different metals, but basically the process is the same every time. A wire is dipped in an electrolyte, and a voltage is applied between the wire and a counter electrode [11]. The voltage - and whether it is AC or DC - depends on the metal and electrolyte used and has to be determined by experiment. Then the oxide layer, whitch appears during the etching, has to be removed by another electrochemical step. This is usually done with a small, negative DC voltage, where the tip is the ground. It is possible to do a further step between the etching and the oxide removal, called micropolishing. This is actually a second etching with an other electrolyte or an acid, and usually a lower voltage. This reduces the diameter of the head of the tip again and produces a smooth surface [2].



(a) A nickel tip etched with a KCl solution. [6]

(b) A Pt/Ir tip etched with $CaCl_2/H_2O/HCl$. [12]

Figure 2.1: Different kinds of tips.

A special method for etching tips is reverse etching [3]. Here the wire is not dipped in the etch solution from above, but instead from underneath. This is carried out with a layer of high-density electrically insulating liquid under the electrolyte. The wire is in this liquid and protudes a little in the electrolyte. This way the tips get an extremely slim shape (see Fig.2.2) [4]. However, because of the setup, doing this kind of etching is a lot more complex then the etching from above.

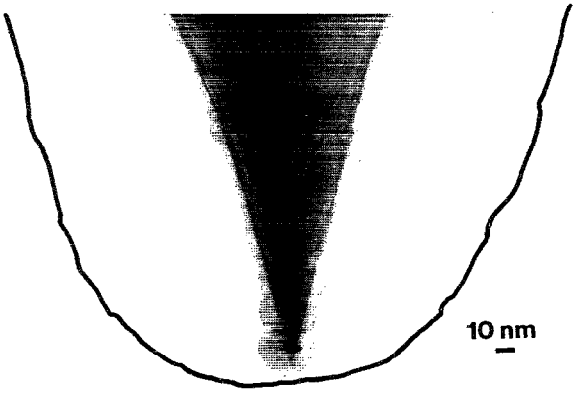


Figure 2.2: A reverse-etched tungsten tip. [3]

2.2 Tips for resistivity measurements.

Sharp tips are also used for resistivity measurements in an SEM [1], where the current distribution of small devices is being measured. To do that, sharp tips are mounted in micromanipulators, are installed in an SEM. The tips are placed on the device, to make electrical contact, a voltage is applied and the drop measured. In general, there are two ways to make these measurements: first the normal resistivity measurement with two tips, and secondly the four point resistivity measurement. For the four point measurement the tips are placed in a row, a current applied between the two outer tips and the voltage drop measured between the two inner tips (see Fig.2.3). In addition, the problem with this measurement is the tips. As mentioned in chapter 1 they bend when they are landed on a sample (see Fig.2.4). Because it can only be estimated where the tips make contact, it is that way a relatively inaccurate measurement. For further information concerning this method, visit the hompage of the Institute of Solid State Physics from the TU Graz [1].

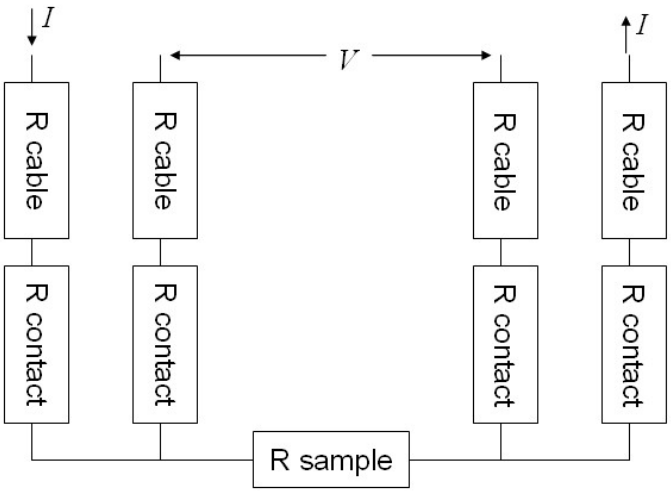


Figure 2.3: Diagram of a four point measurement [1].

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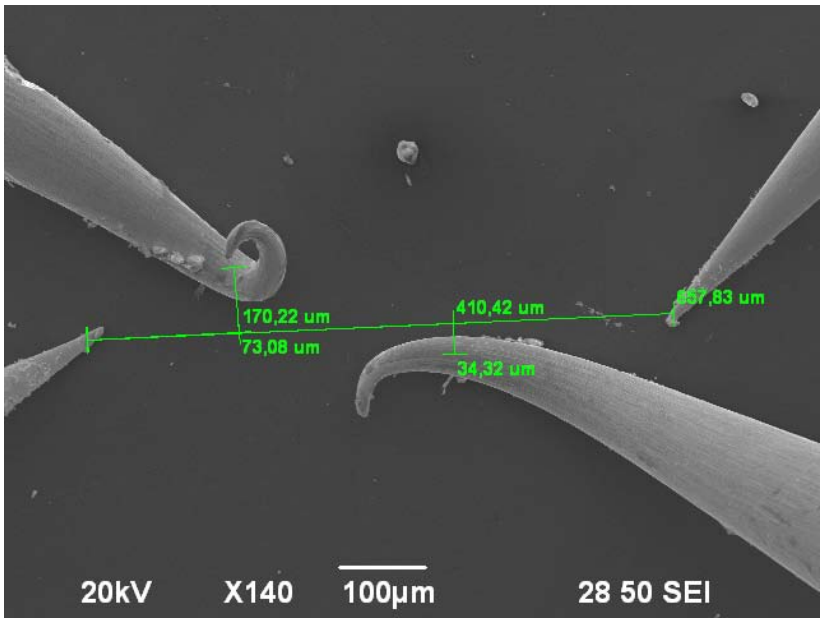


Figure 2.4: Four point measurement with four Pt/Ir tips produced during the project.

One kind of measurement avoiding the bending problem is the spreading resistance profiling, in short "'SRP"'. The sample is ground diagonally and two tips with a constant distance are pressed rectangular to the surface on the sample with one million pounds per sq inch [7], so that they mechanically deform the sample surface (see Fig.2.5). But the SRP is only good for making measurements of carrier concentration in semiconductors like silicon or germanium, so for making measurements on with sharp tips, the resistivity measurement has to be used.

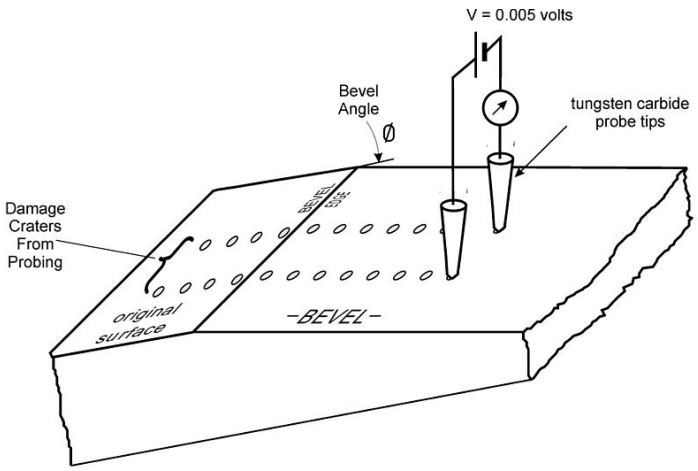


Figure 2.5: Illustration of the spreading resistance profiling [7].

3 Experimental methods

3.1 Spot welding

A short piece of 100 μm thick Pt/Ir wire was spot welded at the end of a tungsten wire. The tungsten wires used were 0.5 mm in diameter and between 2 and 4 cm long. The welding was done at two spots (Fig. 3.1) to make sure that the Pt/Ir wire was fixed on the tungsten and that there was good electrical contact. The wire was cut so that a 2 to 3 mm long piece was left over for the etching step.

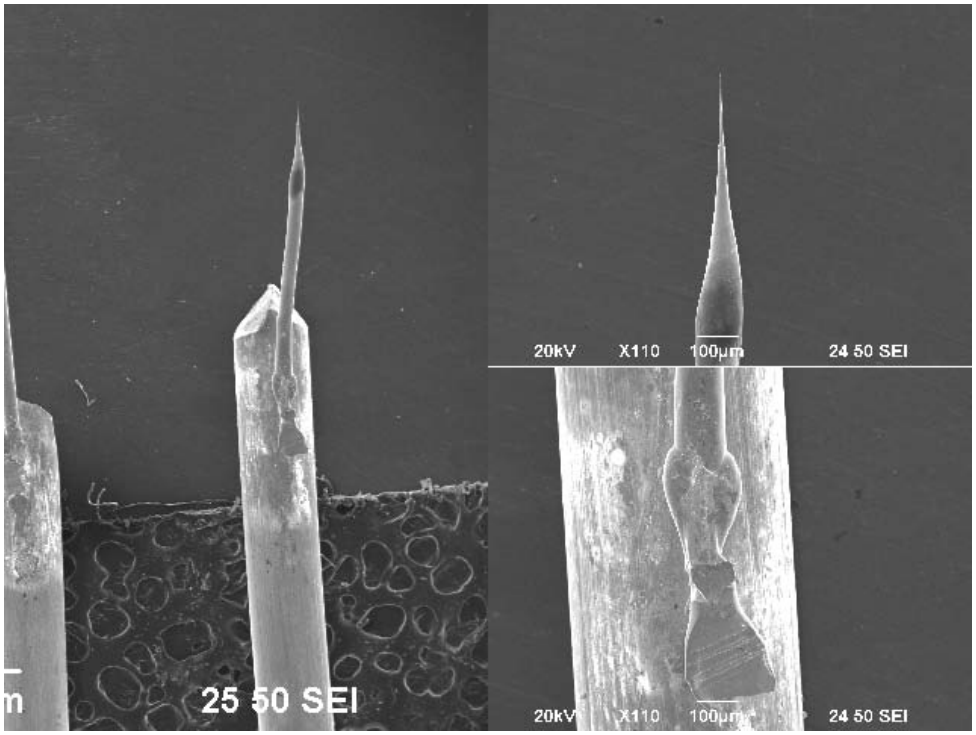


Figure 3.1: A finished tip.

3.2 Etching

The electrochemical etching was done with a $CaCl_2/H_2O$/acetone solution [2], namely 20 ml distilled water with 20 ml acetone and 7g calcium chloride dihydrate. The solution was over-saturated with acetone, in order to create a thin film of acetone swimming on the top of the solution. Using a syringe to put the solution from the storage bottle into the the box where the etching was done, ensures that there will not be an acetone film which could influence the process.

For the etching, the Pt/Ir wire should be dipped in the solution about 1 mm deep. It is not important that the wire is dipped in perpendicular to the fluid surface. A graphite rods was used as the counter electrode [8](Fig. 3.2). Experiments with copper

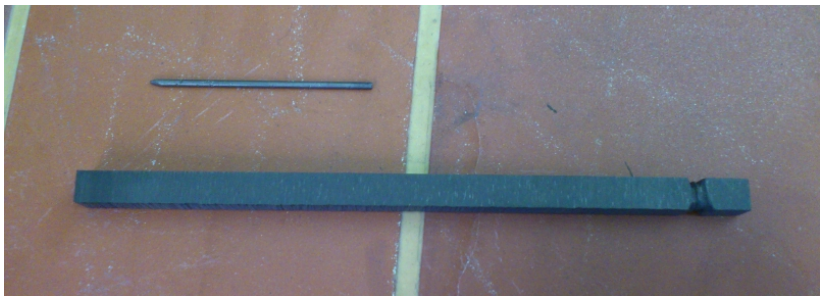


Figure 3.2: The graphite electrode (the big one) and the pencil lead (the small one).

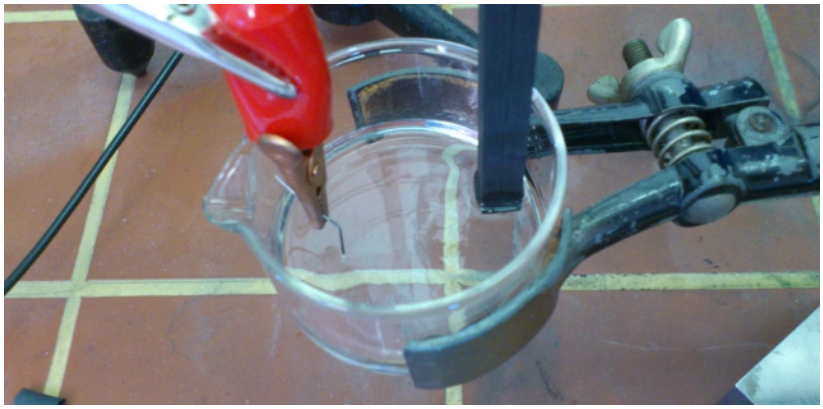


Figure 3.3: The setup for the etching. Bubbles can be seen appearing as a white shape around the tip.

and steel as the counter electrode did not yield the desired results. Using these metals, an oxide layer appeared and because of the change of the resistance these etchings were not successful. Etching with the lead of an ordinary pencil as the counter electrode produced almost the same results as with the graphite rod, because pencil leads are made of graphite mixed with clay [9] (see Fig. 3.2). Although the graphite does not react with the $CaCl_2/H_2O$/acetone solution, the electrode has to be cleaned after 10 - 20 etchings. Usually it is sufficient to flush it with distilled water. During the etching process PtCl is formed. That is a black precipitate which adheres to the graphite. The influence of PtCl depostits on the resistivity of the graphite was not measured, but when the graphite electrode, after 20 etchings, was put in a fresh solution, a black cloud appeared around the electrode.

For the electrochemical etching a sinusoidal voltage was applied between -20 and 20 V at 40 Hz [2]. The etching had to be stopped when the current intensity fell below 20 mA. For our setup, a Keithley Source Meter 2636 A was used as the voltage source. The program used for the etching can be found in Appendix A4.2.

During the etching bubbles can bee seen appearing around the Pt/It wire. Because of the acetone in the solution, they stay very small (around 0.1 mm) [2]. But after etching a few tips the solution becomes more viscous and thereby the bubbles bigger and more stable. It turned out that when the viscosity of the solution exceeds a certain value, the bubbles became so big and stable, that the contact between the tip and the

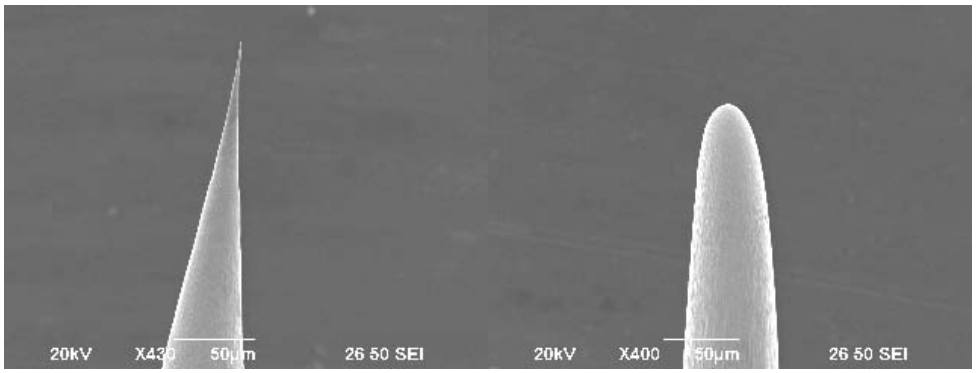


Figure 3.4: A well etched tip compared to a tip etched with an over-used $CaCl_2/H_2O$/acetone solution.

solution is no longer the surface of the solution, but rather the membrane of one or more bubbles. That means that the contact is higher than the solution surface and thereby the sharp part of the tip is etched away. Such a tip is shown in Fig. 3.4. How many tips can be etched before changing the solution depends on how deep the Pt/Ir wire is dipped into the solution, so on how much material is etched away. For etching 4 tips which were dipped in the wire about 1 mm, a solution of 17 - 20 ml was used. It wasn't possible to make more than 5 tips without changing the solution.

After etching, the tips should be cleaned with distilled water. They should be dipped in a bowl filled with water, and moved left and right a little bit. If done carefully, they can be flushed, if the water is allowed to flow too quickly while flushing, the tips can easily be bent.

After the etching step the tips are usually around 200 nm thick with a slim shape(see Fig. 3.5).

3.3 Annealing

The annealing is carried out for two reasons. Firstly, the surface of the tip after the etching is not very smooth (see Fig. 3.5). But more importantly, the heating of the tip reduces the amount of dislocations in the Pt/Ir, and thereby the grains in the material get bigger [2]. Thus the elastic properties of the tip are changing. An unannealed tip just bends if it is pressed on a surface. This will be discussed in section 4.1.

The annealing was done with a bunsen-burner, the wire was heated to red-heat for 10 - 20 s. This step slightly enlarged the diameter of the tip (see Fig. 3.6).

Test of the elastic properties were tested by bending one tip at the right edge of the silicon sample which was in the SEM at this time (see Fig. 3.7). The elastic properties were not as bad as expected. The tip was deformed, but after taking the tip away from the silicon it bent back to a certain value.

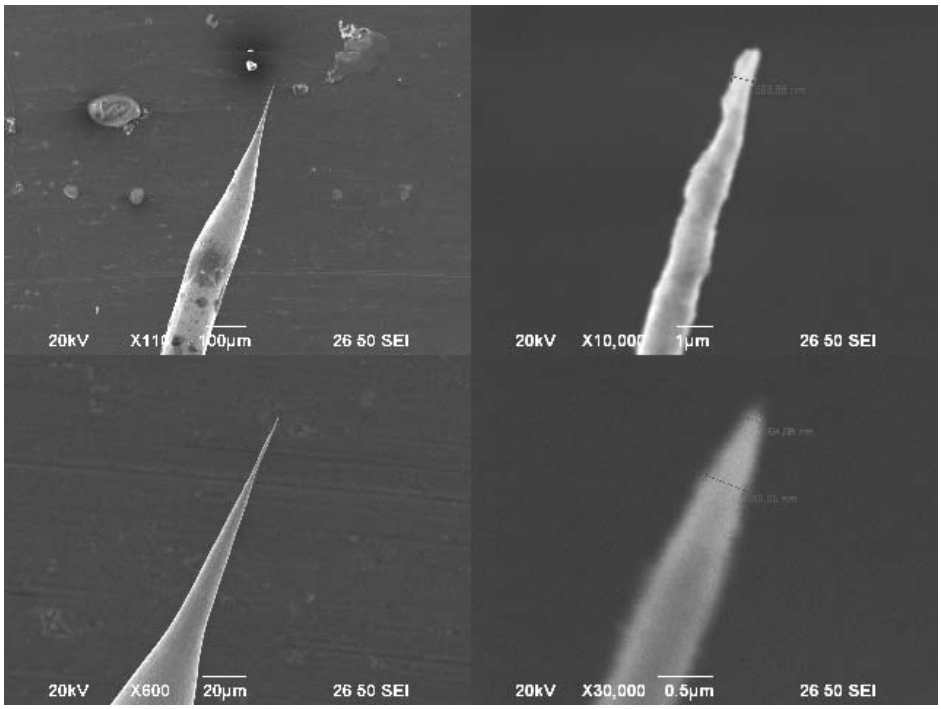


Figure 3.5: Two tips after the etching step. The right picture shows the same tip as the left with higher magnification.

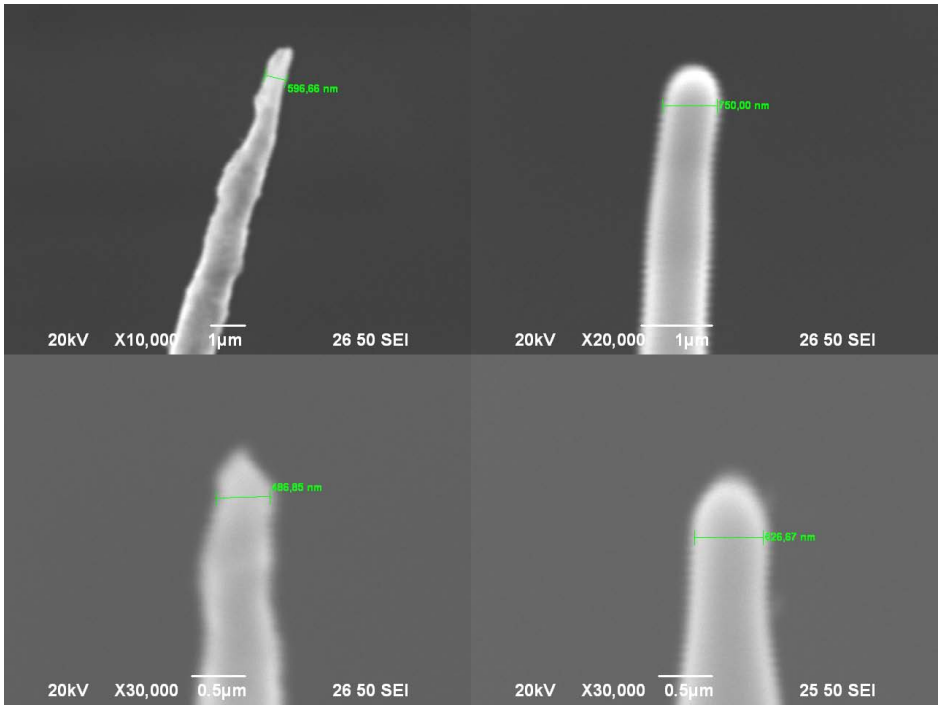


Figure 3.6: Two tips before and after the annealing step. The pictures on the right show the same tips as on the left but with higher magnification

The tips should be cleaned again after the annealing as with the etching (Section 3.2).

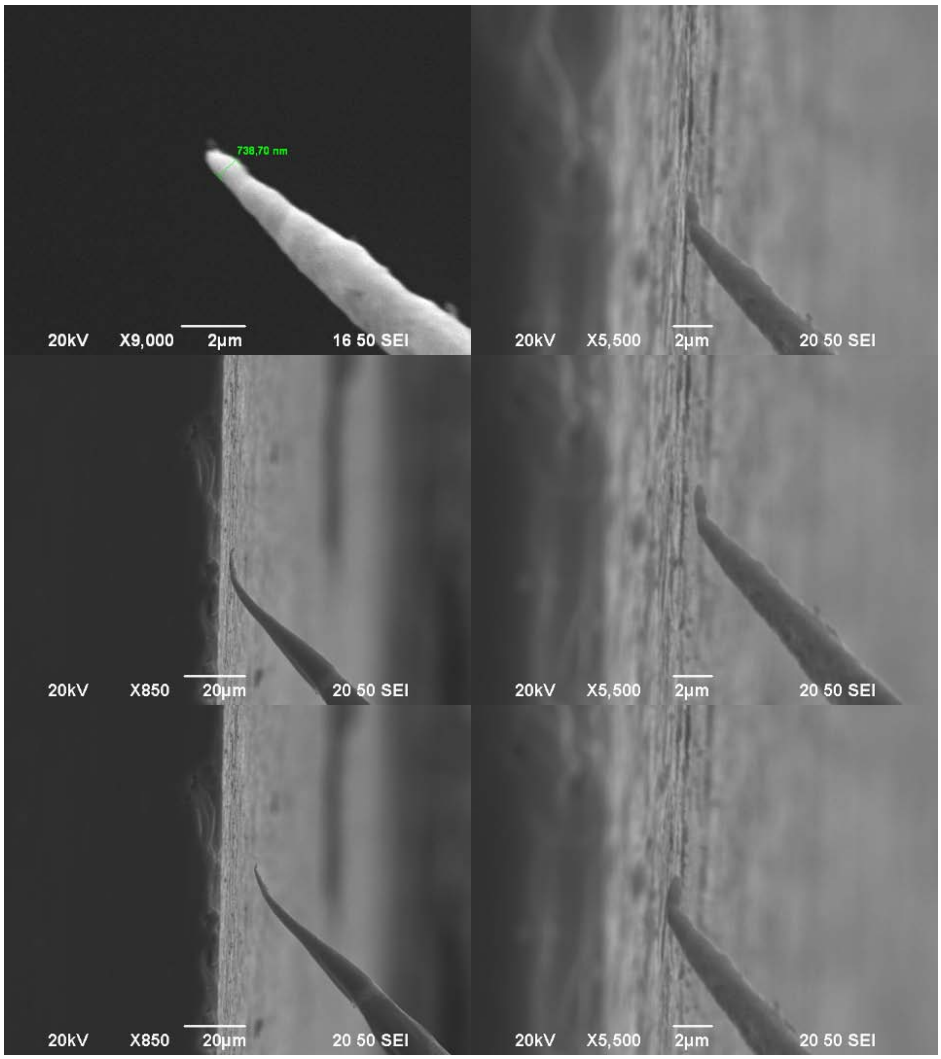


Figure 3.7: Test of the elastic properties of an annealed tip. The upper left picture shows the tip before the bending. The three pictures on the right show two careful crashes, and the two lower on the left a brutal crash on the silicon.

3.4 Micropolishing

To reduce the diameter of the tip after the annealing and keep the surface smooth, an electrochemical micropolishing was done [2]. See Fig. 3.8 for the result. The microwire was etched with an H_2SO_4 solution diluted to 1% with distilled water. A gold wire-loop, with 4 mm in diameter, was dipped into the solution so that a thin film appeared. The gold wire was mounted in a micromanipulator and under a optical microscope it was moved so that the microwire was in contact with the H_2SO_4 film (see Fig. 3.9). Because of the capillary action [10] the film coated the whole microwire.

For the micropolishing a 3 V square wave voltage at 1kHz was applied for 12 s. The electrodes were the tip and the gold wire. During the micropolishing it was possible to see bubbles appearing around the microwire, sometimes even without the microscope. It turned out, that this is not an indicator of the quality of the reaction if the bubbles are big. Sometimes it is an indication for that the contact between the H_2SO_4 film

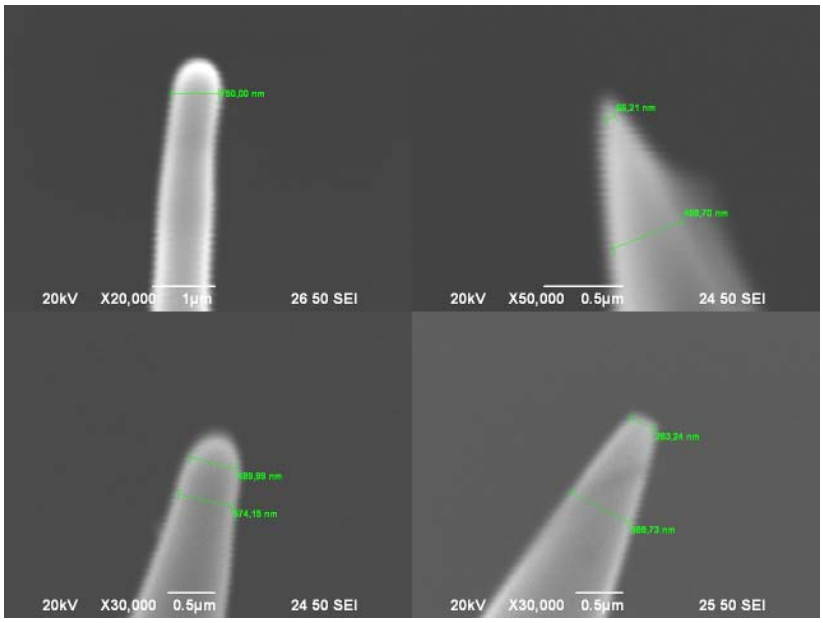


Figure 3.8: Two tips before (left) and after (right) the micropolishing.

and the tip is not at the microwire, but at the "thicker" part, where more material is etched away. That might mean that the microwire loses contact with the film and protrudes on the other side. This can be seen using a microscope and focusing on the tip. There is no problem when moving the gold-loop back and forth a bit during the micropolishing to make sure that the microwire is being polished completely, or to polish some of the "thick" part to make grain boundary visible (Fig. 4.2) - this will be discussed in section 4.1.

There is a problem, however, with the lifespan of the H_2SO_4 film. If there is only a gold loop it does not last long enough to finish the polishing. To have a longer lifespan, the loop has to be at the end of a twisted part (ours was 1.5 cm long - see Fig. 3.9), and the wire has to be tilted, so that the loop is below. The wire has to be dipped into the H_2SO_4 solution completely, so that there is enough solution available at the twisted part to keep the film existing. This way the lifespan is about 1 - 2 min.

It is not necessary to clean the tips after the polishing if the next step is done immediately afterwords. If there is a break in between which is long enough for the tips to dry, it's better to clean them afterwords, as with the etching (Section 3.2) and the annealing (Section 3.3).

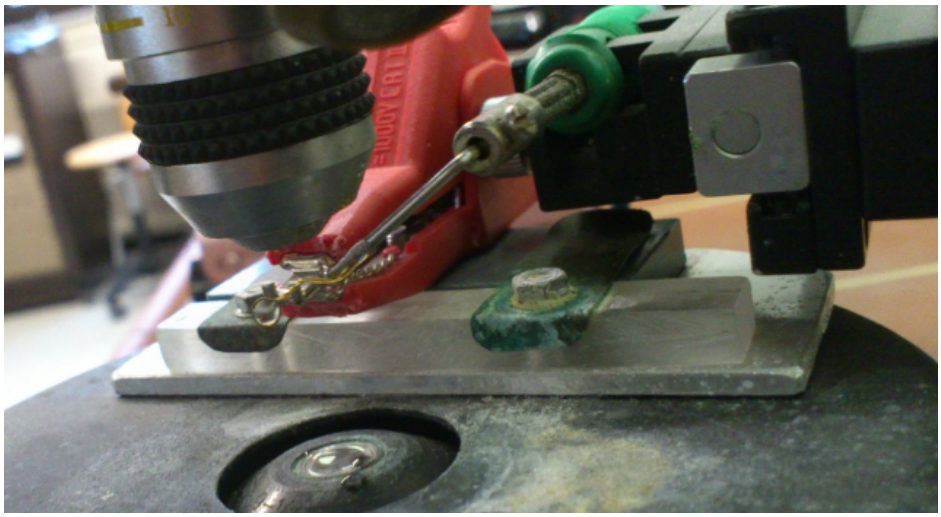


Figure 3.9: The setup for the micropolishing. The gold wire with the H_2SO_4 film can be seen; when the picture was taken there was no contact between the film and the microwire.

3.5 Removing the oxide - "reverse polishing"

The micropolishing causes oxidation of the platinum [2]. The oxide layer prevents electrical contact with the tip, so it has to be removed. To do that, the tip hast to be put in the same setup as in the micropolishing step, and a -1.1 DC voltage applied for 2 min [2]. The ground has to be at the gold wire. During the process bubbles appear again, but a lot smaller than during the micropolishing. Here they can be seen only through the microscope and they slowly decrease with time. But when the oxide layer is removed, etching of the platinum should be continued slowly so that the occurrence of bubbles does not stop after the oxide is gone. After 2 min reverse polishing there was good electrical contact between all tips. The tips also became a little sharper after removing the oxide layer (Fig. 3.10).

Because this is the last step, the tips had to be cleaned afterwords with distilled water, as with the annealing and the etcing (see section 3.2).

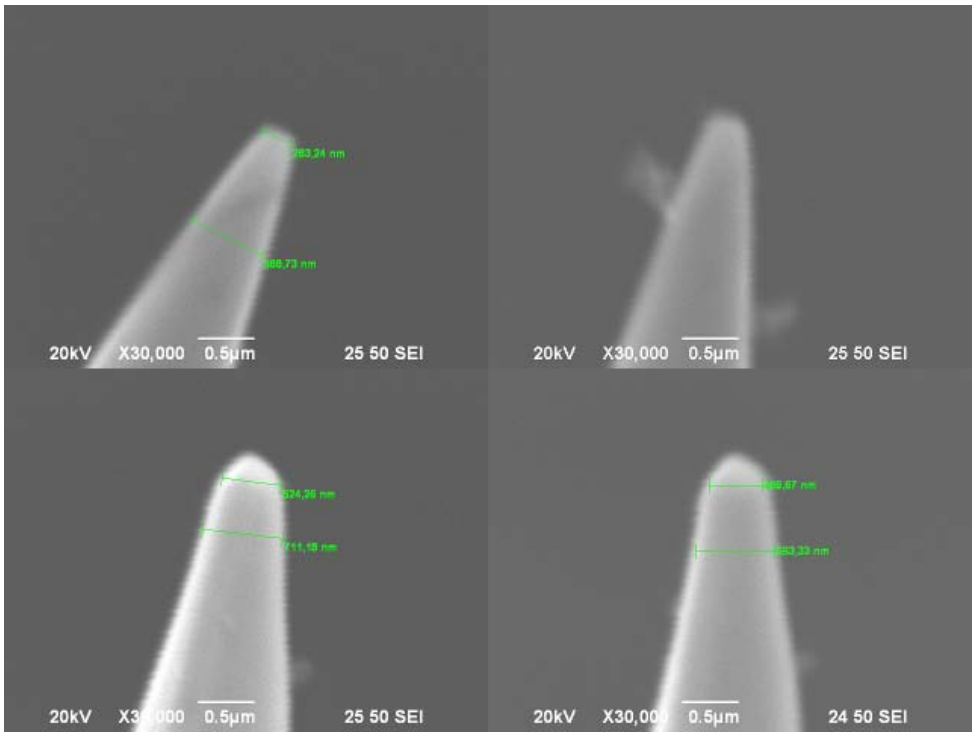


Figure 3.10: Two tips before (left) and after (right) the removal of the oxide layer.

4 Tip properties

4.1 Elastic properties

One of the main intentions of the project was to produce flexible tips, so that after pressing them on the sample surface they return back to their former shape. The crucial step for this property is the annealing. Before that the tips have very little flexibility, they just bend (see Fig.4.1). After the annealing, the tips get some flexibility (Fig.3.7), but for making electrical measurements they have to be pressed so hard on the surface that they still get bent. So in this respect the same problem occured as with the tungsten tips.

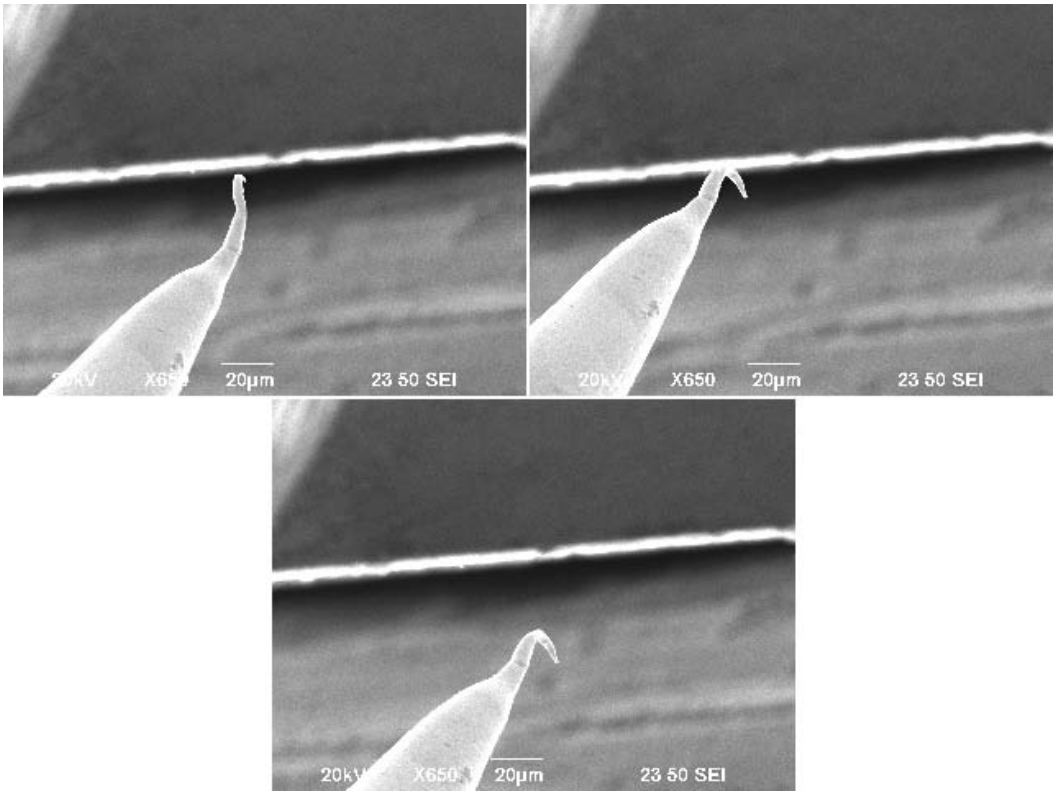


Figure 4.1: Test of the elastic properties of an unannealed tip.

The reason for the change of the properties is that the amount of dislocations in the Pt/Ir is reduced during the annealing, so the micro-crystals (grains) get bigger. The longer the annealing is done the bigger the grains should be; however, this was not observed in great detail, so a relation between grain size and endurance of the annealing cannot be given. After the micropolishing of an annealed tip the grain boundaries are visible (see Fig.4.2). They can be seen on one hand because of their different color, and on the other because they are separated by thin lines, as clearly shown on the right, upper picture in Fig.4.2. In the best case the micro-wire should be a single micro-crystal, it wasn't possible for us to prove that, because the resolution of our

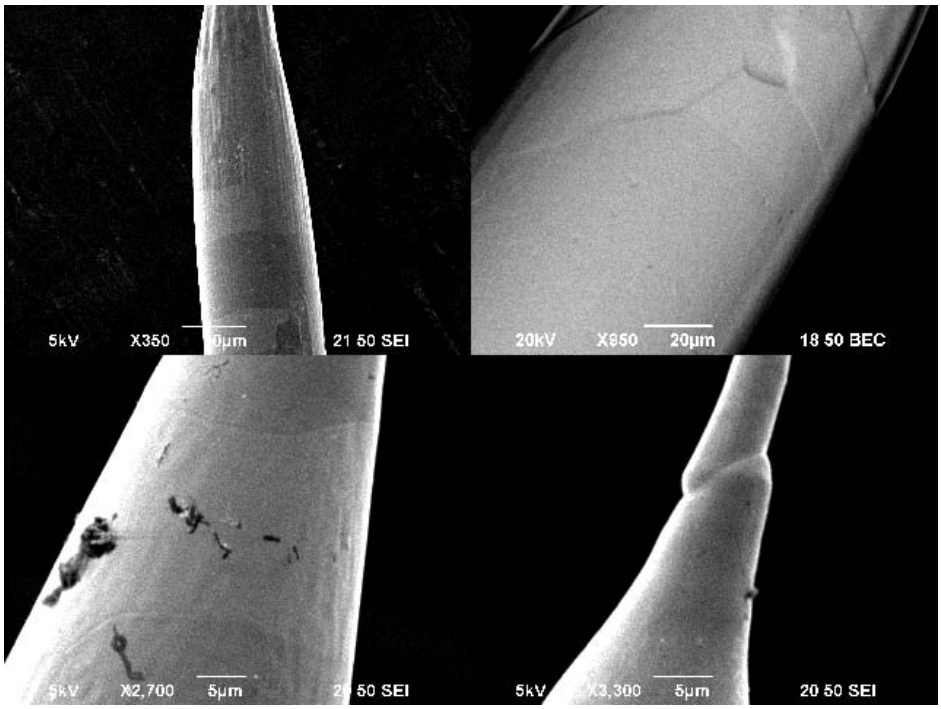


Figure 4.2: Grain boundaries after the micropolishing. The upper right picture was taken with the back scattering detector, the others with 5kV acceleration voltage. On the lower pictures the same tip is shown; the picture on the right shows that there is a grain boundary at the point the micro-wire begins.

SEM was insufficient. In the right, lower picture a grain boundary can be seen at the point where the micro-wire begins. We expected to see smaller grains on micropolished unannealed tips, but we did not (Fig.4.3).

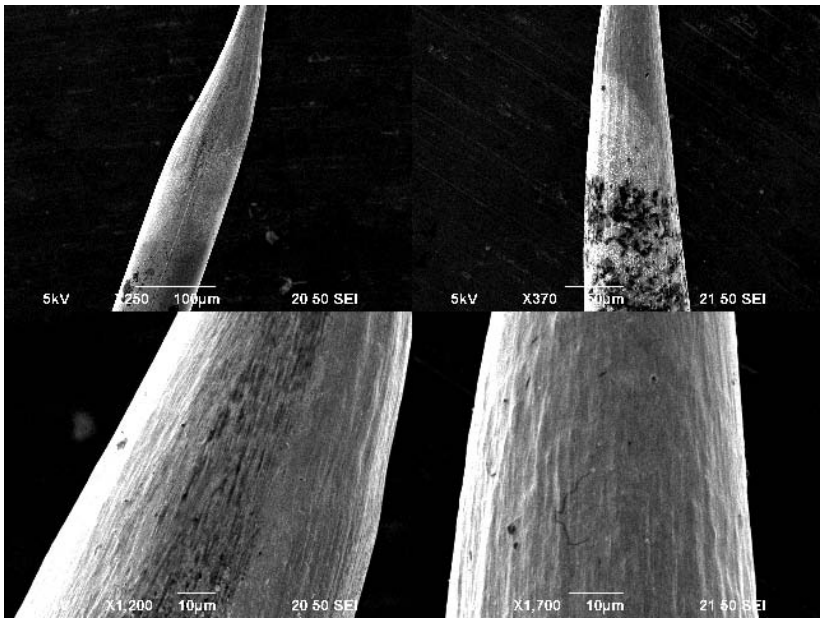


Figure 4.3: The surface of two micropolished, unannealed tips. It is not possible to locate any grain boundaries on the surface.

4.2 Electrical properties

Because the tips are to be used for electrical measurements, the electrical properties of the tips have been studied. The resistivity between two tips is about 30 - 50 Ω, if the oxide layer has been removed. If there is an oxide layer, there is a bigger chance of melting the tip than breaking through the oxide. More important though is the contact to the sample. It was impossible to create such a contact. Fig.4.4 showns two EBIC measurements of two PT/It tips in contact with a silicon sample. It can be seen that the contact between the tip and the sample is not at the head of the tip. Three IV curves are shown in Fig.4.5.

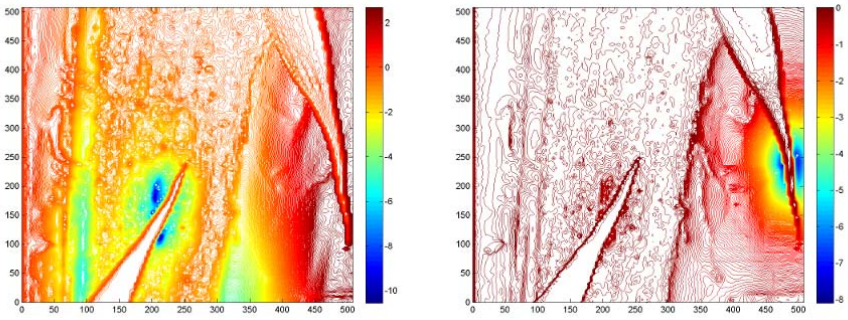
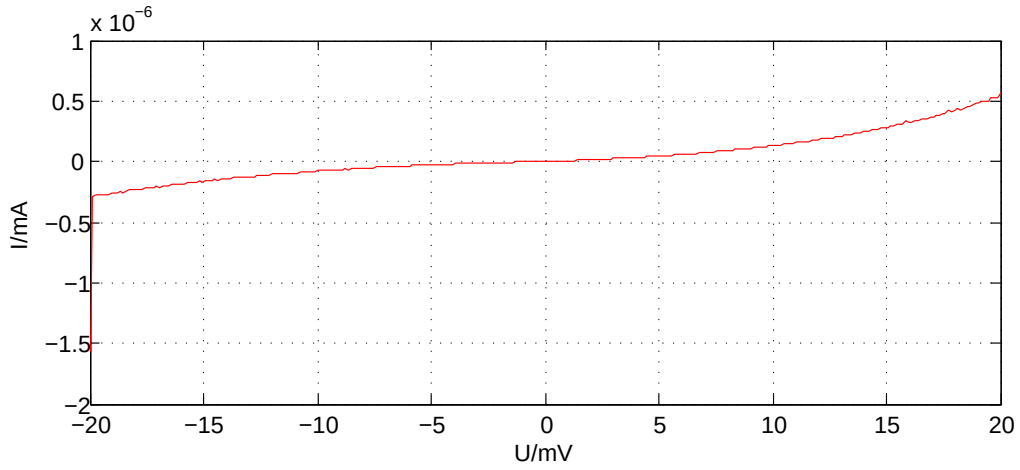


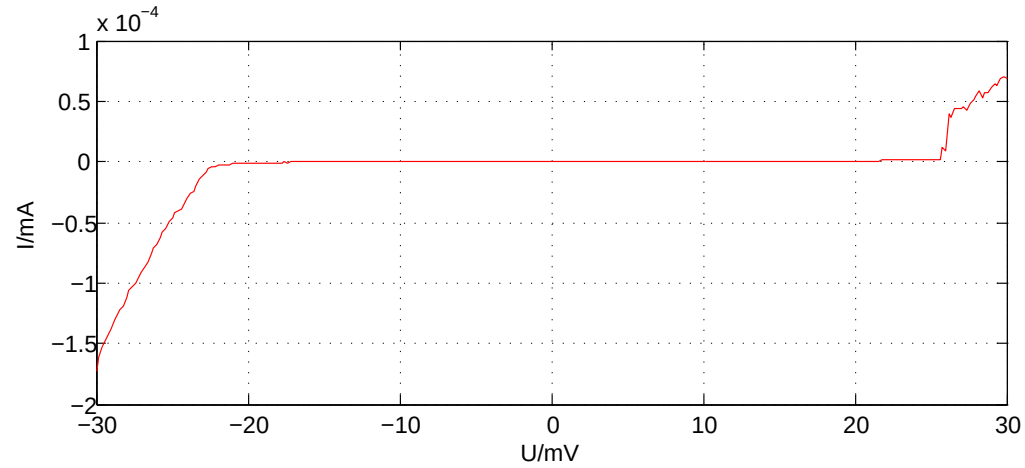
Figure 4.4: EBIC measurement of two Pt/Ir tips on a silicon sample. A separate EBIC measurement was made for each tip. For an unknown reason both tips could not be measured at the particular time. For the corresponding IV curves see Fig.4.5.

We also tried to electroform the tips, in order to melt them onto the silicon sample. But the voltage source used was unable to produce a high-enough voltage. The highest voltage applied was 200 V.

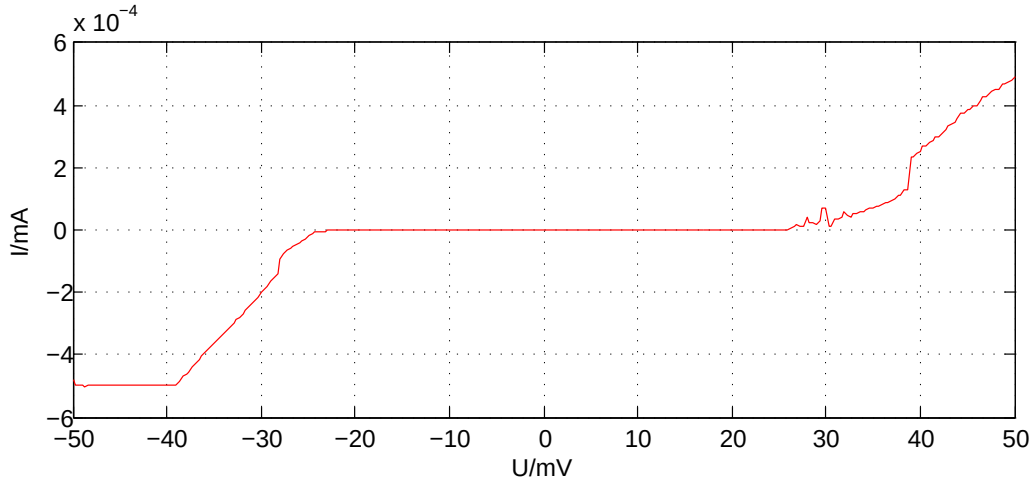
Compared with the industrially manufactured tungsten tips, the electrical properties between two tips are more or less the same, but with tungsten tips better contact with a sample can be made. That is because on the one hand tungsten is a a much harder material than platinum, and on the other hand, the industrially manufactured tungsten tips are thicker than our home-made Pt/It tips, so they are more stable. We could have tried to make contact with a comparable thick Pt/Ir tip, but that would not have been reasonable, because we wanted to have sharper tips so that we would know more precisely where the contact with the sample was made. With Pt/It tips the same size as the tungsten tips, there would also be the same problem. Probably it would be even greater because Pt/It is not as hard as tungsten, and moreover, platinum is more expensive than tungsten. So one could try to make very sharp tungsten or even silicon tips [5].



(a) 1^{st} IV



(b) 2^{nd} IV



(c) 3^{rd} IV

Figure 4.5: Three IV curves of two Pt/Ir tips. They were always at the same position. For the corresponding EBIC see Fig.4.4

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Sine loop program for the etching

```
amp_v = 1000
m_delay = 0.001
list_v = {0.309, 0.588, 0.809, 0.951, 1, 0.951, 0.809, 0.588, 0.309,
 -0.309, -0.588, -0.809, -0.951, -1, -0.951, -0.809, -0.588, -0.309}

------------------config SMU A-------------------------
smua.reset()
smua.measure.autorangei = smua.AUTORANGE_ON
smua.source.func = smua.OUTPUT_DCVOLTS
smua.source.levelv = 0
smua.source.limiti = 50e-3
smua.measure.nplc = 0.001

smua.nvbuffer1.clear()
smua.nvbuffer1.appendmode = 1
smua.nvbuffer1.collectsourcevalues = 1

smua.nvbuffer2.clear()
smua.nvbuffer2.appendmode = 1
smua.nvbuffer2.collectsourcevalues = 1

smua.measure.count = 1

display.smua.measure.func = display.MEASURE_DCAMPS

-----------------measurement-----------------------
smua.source.output = smua.OUTPUT_ON

   smua.measure.delay = m_delay
   i = 1
   reading = 1

   repeat
    smua.source.levelv = math.sin(i)*20
        delay(0.0008)
        i = i + 0.25
        if i > 360 then
            i = 1
    end
    if i == 90 then
        reading = smua.measure.i()
        print(reading)
    end
   until reading < 0.020
```