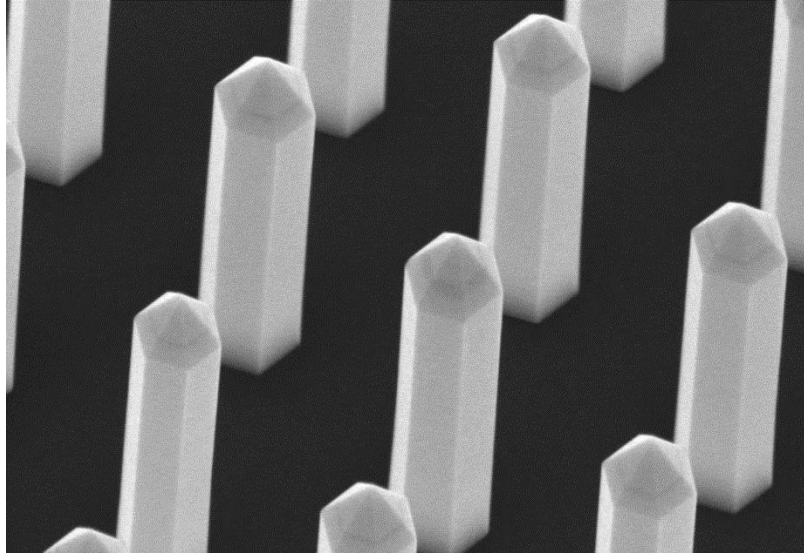


# SCANNING PROBE MICROSCOPY WITH GALLIUM NITRIDE NANOWIRES



MASTER THESIS IN ENGINEERING NANOSCIENCE

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## **Abstract**

In scanning probe microscopy the properties of the tip is crucial in determining which information that can be obtained from the resulting images and spectroscopy. Ordinarily metal tips are used for scanning, however by using semiconducting nanowires as tips one would have very well defined probes with more advanced possibilities for spectroscopic measurements. However, currently creating such high precision and advanced scanning probe tips has been expensive and time consuming.

GaN nanowires would be excellent candidates for semiconductor tips since they can have sharp end points and are hard. A method for quickly creating STM tips from large arrays of GaN nanowires has been developed. The basic principle of the method is to apply a conductive glue to readily available blunt tungsten tips and bring them in contact with an array of nanowires. A large number of different methods for fabricating the complete tips with the attached nanowires were evaluated. For the initial evaluation Scanning Electron Microscopy (SEM) and optical microscopy was employed in the clean room facilities in Lund. Many process variables were evaluated at room temperature including glue type, tungsten tip shape, wire preparation and method for transferring wires. Finally the yield of useable tips for the STM was found to be one out of three with optimum methods. The time for creating one of these tips was 15 minutes, a significant improvement on other methods for creating nanowire probes.

The new tips were then tested in a Scanning Tunneling Microscope (STM) on a thin atomically flat Au metal film. Scanning tunneling spectroscopy measurements gave the expected current to voltage characteristics from a tunneling contact between GaN and Au. These tests showed that imaging with the tips is possible, but compared to measurements performed also with ordinary metal tips on similar substrates, obtaining high resolution was more difficult and the tips were less mechanically stable.

## **Acknowledgements**

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## 1. Introduction

Microscopy is the art of making things that are otherwise not visible to the naked eye visible. The greek origin of the word microscopy means “to view small things”. With the invention of glass came the first lenses and they allowed humans to view and examine small details of the world around them. In the 16th century two spectacle-makers experimented with combining several lenses in a tube. The combination increased the magnification above that of a regular single lens and this is the first known example of what we today call a microscope.

Since then the light microscope has evolved into several different microscopy techniques. As the technology pushed the boundaries of what could be observed with visible light, new microscopy techniques were invented to probe further into the unknown.

These new microscopy techniques have allowed us to observe individual atoms and one of the youngest of these new techniques is called scanning probe microscopy (SPM), which in its most basic form mimics that of the blind man and his cane. It taps a sample with a tiny needle and the movements of the needle is translated into an image of the surface of the sample. The basic setup for this kind of microscope, called an atomic force microscope (AFM) is shown in figure 1.

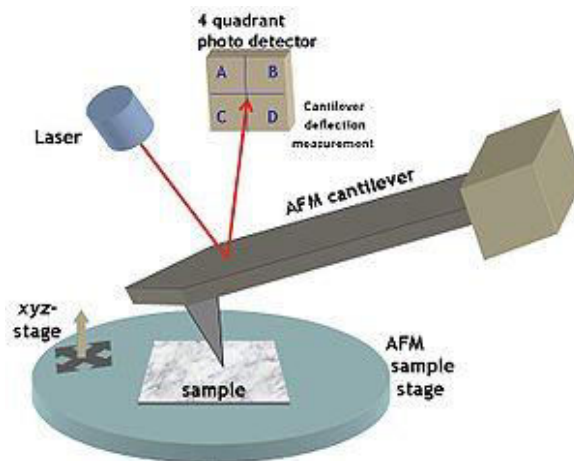


Figure 1. Basic setup of an AFM [1]

A common factor for all SPM microscopes is that the image quality is significantly related to the quality of the tip. With a good tip and the correct settings the microscopes can achieve atomic resolution. This is one of the major advantage of SPM as few other microscopy techniques allow direct measurements on single atoms.

One of the techniques of SPM is the scanning tunneling microscope (STM) that utilizes a conducting tip to measure the miniscule tunneling current between the tip and sample surface. This technique allows examination of several features related to the electrical conductivity without requiring a physical contact with the sample.

A regular STM uses a metal tip and performs scanning on a conducting sample as the conductivity of the sample is necessary to measure a current, as a result the samples can be either metals or semiconductors. Scanning on semiconductor samples to examine the band gap and surface electron states is common.

Semiconductors are materials whose electrical conductivity can be manipulated and this is why they have become the cornerstone of modern computer chip technology, solar panels and light emitting diodes (LED).

One of the defining features of a semiconductor is its band gap, which is the amount of energy required to excite an electron from a occupied state to a conductive state. The excited electrons can also return to their original state by emitting a photon corresponding to the energy difference between the states. This is the basic principle behind the light emitting diode and there is considerable research in creating semiconductors that have a desirable band gap for emitting visible light. The Nobel prize in physics of 2014 was awarded to the research and development of gallium nitride (GaN) LEDs that emit light in the blue to ultraviolet spectra [2]. The development of cheap and high quality blue LEDs was a requirement for producing diodes that emit white light. The main advantage of LEDs are their superior energy efficiency compared to regular incandescent lightbulbs. A modern LED which contains the three major colors red, green and blue to produce all visible colors is shown in figure 2.



*Figure 2. The inside of a diode with three smaller LEDs [3].*

We aim to create STM probe tips with GaN nanowires as the scanning medium and investigate the possibilities with semiconductor on semiconductor STM measurements. We chose GaN as the nanometer consortium in Lund has a well developed method for growing GaN nanowires with very precise dimensions and sharp tip ends.

Scanning with a semiconductor tip would allow for selective imaging of electron surface states in metals and semiconductors that would not be possible with a metal tip [4]. It may also be possible to use the GaN tips as light wave guides during scanning and perform simultaneous electrical and light microscopy similar to near-field optical microscopy with metal probes [5].

The first step to achieve this goal is to develop a manufacturing method of nanowire tips for use in the STM. Preferably this method should be as quick and cheap as possible so the manufacturing of the tips is not the limiting factor in the overall project. Usually a significant number of tips is used in a STM project.

This is the goal of the project presented in this paper, to find a manufacturing method that does not require expensive equipment or several hours of work for an individual tip and has a reasonable yield of functioning tips.

One of the most common ways of creating tips for STM measurements is chemical etching of tungsten wire [5]. This creates a fine tip, but the process is quite inaccurate and the tip form varies each time which increases the probability for tip related artifacts. This etching does not work for compound semiconductors, if one wants well defined tips as we have with the nanowires.

There are other methods for creating extremely fine and defined tips, like high precision ion milling of tungsten wires [6]. These methods are time consuming and expensive compared to the chemical etching. The lifetime of a high quality tip is highly dependent on how the user treats the tip and what material is being scanned, but generally several tips are used during an STM project. As a result of this the high precision methods are inefficient when the goal is to do regular experiments, as more time will be spent creating tips than imaging with them.

Nanowires are attractive as tips as they can be grown to very precise dimensions in large quantities. Each growth sample of GaN nanowires contain millions of nanowires. Because of this the potential amount of tips from each nanowire sample is high.

There are several methods presented in literature on how to fabricate nanowire tips. A method with high precision is drilling a hole in a STM tip with a focused ion beam and then picking up a single nanowire and fixating it in the hole [7]. Another is growing a lot of nanowires on a flat tip and then milling all but one off with a focused ion beam [8]. A third picks up carbon nanotubes with a tip in an AFM microscope and then coats the carbon nanotubes with nickel to increase its conductivity and stability [9]. All of these methods have the same disadvantages as the high precision tungsten tips as they are time consuming and expensive.

Using semiconductors as tips in STM has been tried before, but not widely adopted as a microscopy method [10]. One method of creating these tips is by breaking a thin wafer of the semiconductor and then fixing one of the shards to a regular tip. With these tips atomic resolution have been achieved which shows promise for improving the tips. But this fabrication method shares the same problem of the chemically etched tungsten tips, where there is little control over the exact tip dimensions, increasing the probability of artifacts.

The basic principle to achieve the project goal is to take blunt tungsten STM tip, which are abundantly available, dip it in glue and then dip it in nanowires. By changing parameters like dipping method and type of glue the best method to quickly create nanowire tips can be evaluated. It doesn't matter if the majority of nanowires picked up does not extend from the tip, as long as at least one wire extends from the surface of the tip it should be usable for STM measurements. The ideal tip created by this process is shown in figure 3.

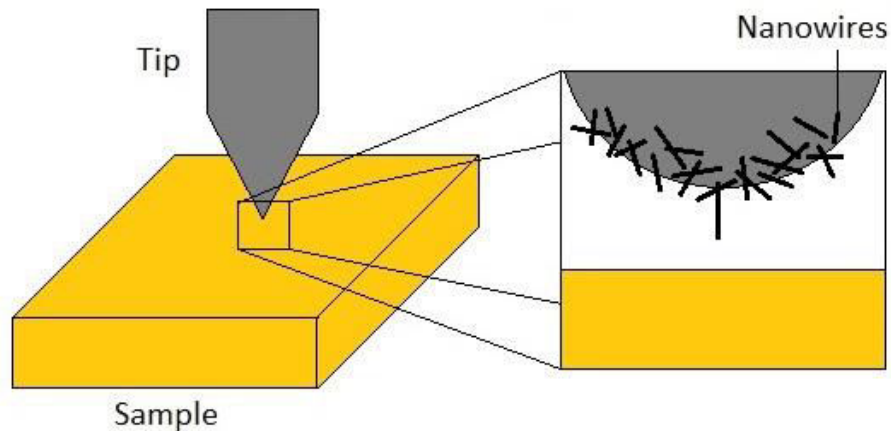


Figure 3. Ideal scenario of a STM tip with nanowires fixated to the end of the tip.

The process was successful in creating tips with nanowires extending from the surface of the tip. There was a significant difference in the reliability of the many different manufacturing methods explored. Of all the different variables tested when creating tips, the type of glue and its application appeared to be the most influential on the finished tips. The process requires additional development and further testing of additional glues to improve the finished tips and the yield of tips with protruding nanowires.

Initial testing in a STM showed that it is possible to achieve imaging with the tips. More work is required for fine tuning of the settings in the microscope to achieve atomic resolution and clear images. Spectroscopy measurements, where the voltage across the tips changes rapidly, appear to have a harmful effect on the tips. Scanning with the GaN tips was possible and reasonable spectroscopy could be done with the tips, but after a couple of spectroscopy measurements a tip was completely cleaned of wires.

## 2. Materials

### 2.1 Semiconductors

When it comes to electrical conductivity in materials, there are three different categories of materials: metals, insulators and semiconductors. The difference between them is the energy required to excite an electron to a state that allows it to conduct electricity. At zero kelvin the electrons of a material are at their lowest possible energy and all states occupied by an electron is called the valence band. The energy states just above the filled electron states make up the conduction band [11].

A metal is a material where the valence band and conduction band have no gap between them without states. The electrons only need a small amount of energy to be excited to an empty state, which allows the material to conduct electricity even at low temperatures.

An insulator has a large energy gap between the bands and exciting electrons across the gap requires a lot of energy and thus it does not conduct electricity well, as few conduction electrons exist.



Semiconductors have a relatively small energy gap between the bands, which allows them to conduct electricity when carriers are thermally excited. Doping can be used to increase the conductivity and control carrier type. This makes them useful from a technological viewpoint, since their conductivity can be manipulated with relatively small means.

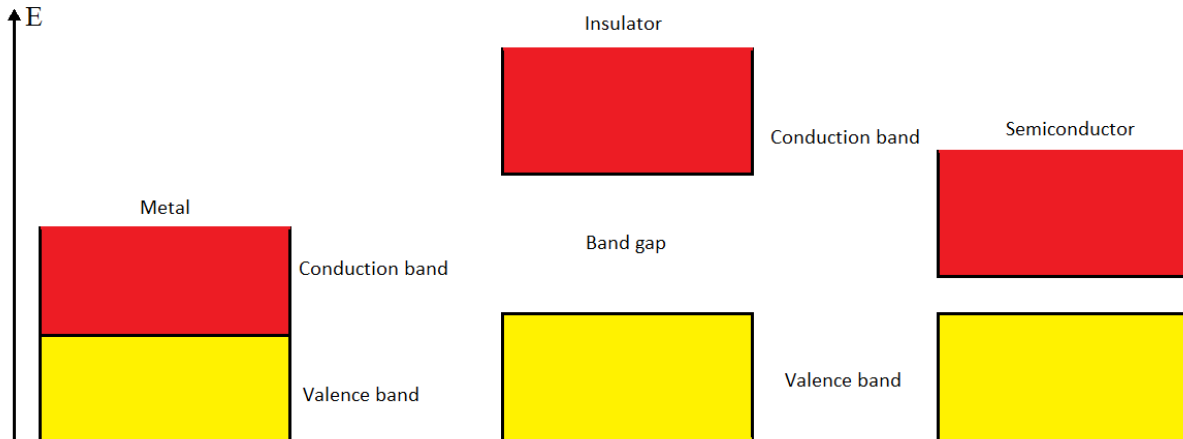


Figure 4. Schematic view of valence and conduction energy levels in different types of materials.

By introducing a small amount of other atoms into a semiconductor its properties can be altered, a procedure called doping. The most common way of doing this is increasing the conductivity by introducing atoms that have one less or one more electron than the native atoms. In the case of doping with extra electrons, it introduces electrons at a higher energy level than the native valence electrons. Thus reducing the energy needed to excite electrons to the conduction band. When doped with atoms with one less electron it creates empty states, called holes, close to the valence band energies. These empty states improves the electrical conductivity by forming carrier holes in the valence band.

The band gap of many semiconductors corresponds to the energy levels of photons in the visible light spectra. This makes them ideal for absorbing and emitting visible light in solar panels and light emitting diodes.

## 2.2 Gallium nitride and III-V materials

Modern computer chips are almost exclusively made of silicon which is a group 4 element with a band gap of 1.12 eV and has a diamond cubic crystal structure that makes it a hard material with a Mohs hardness of 7 [12]. The band gap of silicon is an indirect band gap, meaning electrons have no direct path to get excited or to decay which makes it unsuitable for use in optical electronics. By combining atoms with one less valence electron than silicon (group 3) and atoms with one more electron (group 5), a strong crystal structure like that of silicon can be achieved, with a direct band gap. The advantage of these materials are the crystal structure combined with a variable band gap depending on the atomic species. These materials are called III-V materials and are the major component in modern advanced electronics. Some of these materials, their crystal structure and their band gaps are shown in table 1 below.

Gallium nitride is a III-V semiconductor with a band gap of 3.39 eV, which makes it one of the best materials for emitting blue and ultraviolet light [12]. It is most commonly used in its wurtzite structure and is a very hard material, as seen in the comparison in table 1 below. For comparison 316L stainless steel has a bulk modulus of 152 GPa.

| Material                  | Band gap (eV) | Crystal structure | Bulk Modulus (GPa) |
|---------------------------|---------------|-------------------|--------------------|
| Gallium arsenide (GaAs)   | 1.42          | Zinc blende       | 75.3               |
| Indium phosphide (InP)    | 1.34          | Zinc blende       | 71                 |
| Aluminum nitride (AlN)    | 6.28          | Wurtzite          | 210                |
| Gallium nitride (GaN)     | 3.39          | Wurtzite          | 210                |
| Gallium antimonide (GaSb) | 0.726         | Wurtzite          | 56.3               |
| Indium arsenide (InAs)    | 0.354         | Zinc blende       | 58                 |

Table 1. Examples of III-V materials band gap, crystal structures and bulk modulus at 300 K [12].

## 2.3 Nanowires

Nanowires are structures on the nanoscale that have a large length to width ratio, the usual measure is a width of a few hundred nanometers and a length in the order of micrometers. The small width of the wires limits the lateral mobility of the electrons in the wires and because of this the wires are often referred to as one dimensional structures [11].

Doped semiconductor nanowires have been used to create the logic gates of modern electronics and may be the next step in improving computer chips beyond the capabilities of silicon based chips [15].

Research and development of semiconductor nanowires as high efficiency solar cells utilizing the combined surface area and conductive properties is performed by several different research groups today [16].

## 2.4 Earlier research

Metal nanowire probes for AFM use have been created by electro depositing a large number of metal nanowires on the top of a metal wire. By using a focused ion beam wires are removed until a single wire is left [8]. With this process nanowire tips of several different metals can be manufactured with high precision. This might be applicable with semiconductor nanowires but it is time consuming and expensive to manufacture a single tip with this approach.

Carbon nanotubes have been shown to work as AFM tips with a similar process presented in this report. The process in that report used a silicon AFM tip coated in glue that was dipped in a bundle of single-walled carbon nanotubes. A slower version of this process have also been

demonstrated, where a micromanipulator in a SEM is used to glue or weld a single carbon nanotube to the tip [9]. The carbon nanotube tips proved to have several advantages over traditional silicon AFM tips as the thin tip resulted in better imaging of abrupt edges.

One problem with this technique is that the electrical conductivity of the carbon nanotubes is strongly dependent on the size of the wires. Their behavior has been proved to change between metal and semiconductor with very small changes in size [17]. This demands a significant control of the dimensions of the carbon nanotubes to achieve consistent scanning results in the STM.

STM measurements with a semiconductor tip has been performed with a tip created by cleaving a semiconductor wafer. One of the corners of the wafer is then used as the tip in the microscope [4].

### **3. Scanning tunneling microscopy and scanning tunneling spectroscopy**

#### **3.1 Scanning tunneling microscopy**

STM is a microscopy technique that measures the quantum tunneling current between a thin tip and a sample. The quantum tunneling effect is induced by applying a voltage difference on the tip and sample. Quantum tunneling can be simply explained as particles or waves being able to tunnel across boundaries that would be forbidden to cross in classical physics. In STM measurements electrons tunnel from the sample to the tip, or vice versa, through vacuum. By reducing the distance between the tip and the sample the probability of electrons tunneling is increased to the point where the tunnel current is measurable.

Electrons can only tunnel between the tip and sample when there are free electron states for them to occupy. Because of this the STM does not only measure the topography of the sample, but rather the density of electron states at a specific energy in the band structure.

The scanning tip is controlled by piezoelectric crystals that can move the tip in all three dimensions. While scanning the current through the tip is maintained in a constant state with a feedback loop that moves the tip in the z-direction. By analyzing the resulting voltage on the z-piezo crystal an image of the surface topography is created. This scanning mode is called constant current scanning, another common method of scanning is to keep the height constant and measure the resulting tunneling current as the surface is scanned.

This method reduces noise caused by the movement of the tip but it has problems imaging samples with large height differences since if the distance between the tip and surface is too great there will be no current. The measurements in this project was performed in constant current mode.

A regular STM is operated with a tunneling current at the size of picoamperes ( $10^{-12}$  A). The size of the current is exponentially dependent on the distance between tip and sample, as shown in equation 1, which is a simplification of the more general tunneling theory presented by Binnig in the papers describing the STM [18] [19].

$$I_T \propto V_T \cdot e^{-As\sqrt{\phi}} \quad (1)$$

Where  $I_T$  is the tunneling current,  $V_T$  the applied voltage,  $A$  is a constant with a unit of  $1/\sqrt{J} \cdot m$ ,  $s$  the distance in angstrom and  $\phi$  is the barrier height in eV for tunneling to occur.

In the ideal scenario this will allow the tip to scan the sample with only the single outermost atom, since the tunneling current from atoms one angstrom farther away are an order of magnitude smaller.

In the non-ideal scenario the scan might be performed with a tip that has several atoms as a scanning point which will reduce the lateral resolution. Another non-ideal scenario is when two separate tips acquire a tunneling current from the sample. This will create artifacts in the image which makes features appear twice, this phenomenon is called ghosting [20].

Regular STM is conducted by a metal tip, commonly made of tungsten or platinum-iridium, on a metallized surface. These metals are preferred as they have a high conductivity and a low barrier height for tunneling which makes it easier to achieve good images.

### 3.2 Scanning tunneling spectroscopy

Scanning tunneling Spectroscopy (STS) may be carried out with the STM by varying the applied voltage while the tip is fixed on a location on the sample. The resulting current is measured and plotted versus the voltage in an I-V graph. The graph gives an indication of the density of states at a precise location on the sample.

An ideal spectroscopy with a metal tip on a metal surface with identical work functions at small voltages is displayed in figure 5b.

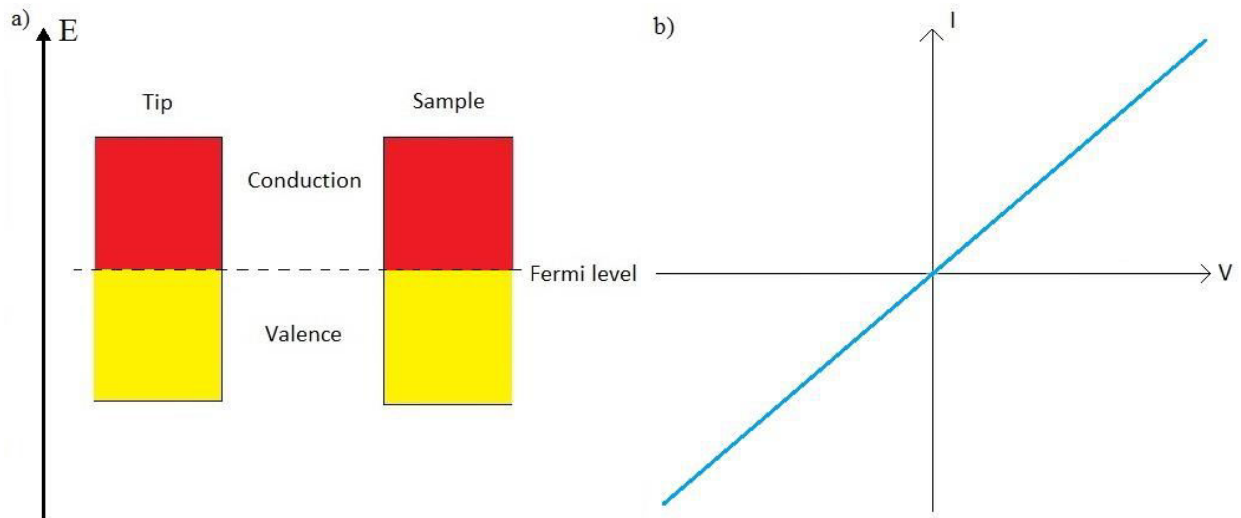


Figure 5a-b. a) Band diagram at 0 V with metal tip and sample. b) I-V graph of an ideal metal on metal spectroscopy measurement

When the voltage is increased/decreased, there are a lot of free states in the metals to allow the electrons to move to and from the tip. The tunneling barrier,  $\phi$  of equation (1), can be

considered a constant resistance  $R$  since the distance is fixed so the resulting tunneling current  $I$  is only dependent on the applied voltage  $U$ , shown in equation 2.

$$I = U/R \quad (2)$$

This gives the current a linear relation to the applied voltage in the ideal scenario.

### 3.3 Semiconductor on metal spectroscopy

With an undoped semiconductor tip scanning on a metal surface or the reverse scenario, the measurements differ from scanning with a metal tip on a metal surface. Without an applied voltage the fermi level of the tip is equal to the middle of the band gap in the semiconductor. This means there will be no tunneling current, since there are no available states in the band gap of the tip for the electrons in the metal to tunnel to. If scanning is done with no applied voltage the tip will crash into the sample when the feedback mechanism aims to reach the tunneling current set point. Because of this effect the voltage must be carefully chosen so that it is larger than half the band gap and accounting for band broadening. Band broadening is an effect that decreases the measured band gap of materials when they are above zero kelvin [18].

Spectroscopy with metal-semiconductor in the ideal scenario will yield zero current until the voltage is enough to allow electrons to tunnel into empty states. When the material is heated above 0K there will be a small probability of tunneling so a small current will be present at small voltages. When the voltage is sufficient for electrons to tunnel to empty states there will be an exponential increase in positive/negative current depending on the voltage, as shown in figure 6b [21] [22].

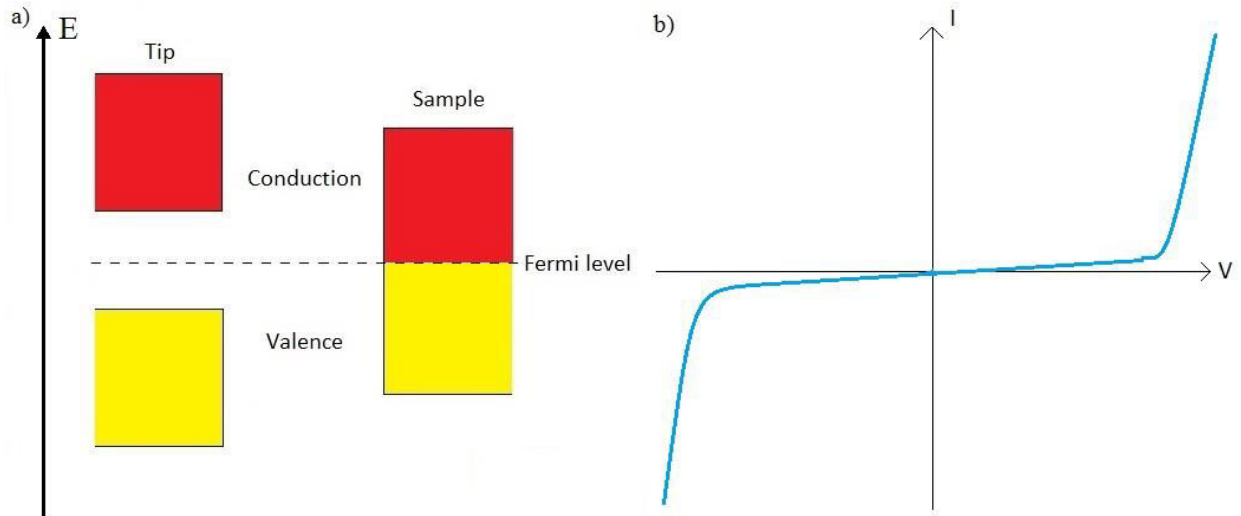
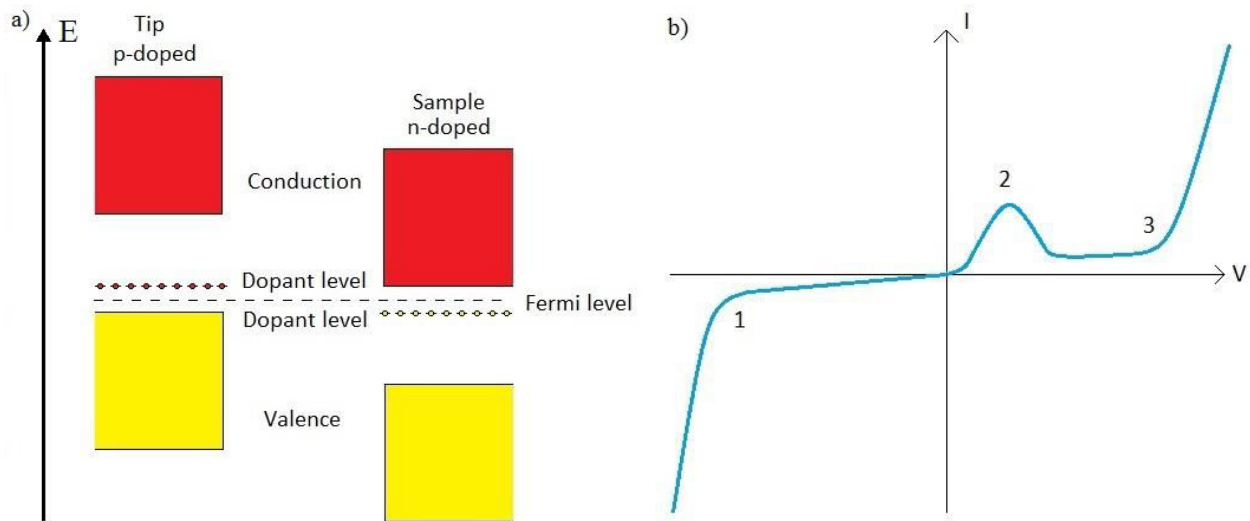


Figure 6a-b. a) Band diagram at 0 V with a semiconductor tip and metal sample. b) I-V graph of an ideal semiconductor on metal spectroscopy measurement

### 3.4 Semiconductor on semiconductor spectroscopy

There is little research done on scanning tunneling microscopy with a semiconductor tip on semiconductor materials. Depending on which semiconductors are used and if they are doped the I-V curves can differ greatly from each other. Since the goal is to achieve a tunneling current, the tip should be doped to increase its conductivity. The I-V characteristics then depends on the sample. A simple scenario with a sample of the same material with the opposite doping as the tip is shown in figure 7.



*Figure 7a-b. a) Band diagram at 0 V with a p-doped semiconductor tip and n-doped semiconductor sample. b) Theoretical I-V graph of a semiconductor on semiconductor spectroscopy measurement.*

The spectroscopy measurements will resemble those of a tunneling diode. When applying a positive voltage to the tip, the energy level of the tip is lowered compared to the sample. At a certain point the dopant levels of the two materials align and a peak in the tunneling current is observed, shown at point 2 in figure 7b. As the voltage increases the dopant levels dealign and the current decreases again until the conduction band of the tip aligns with the dopant levels of the sample and the current increases exponentially, shown at point 3 in figure 7b .

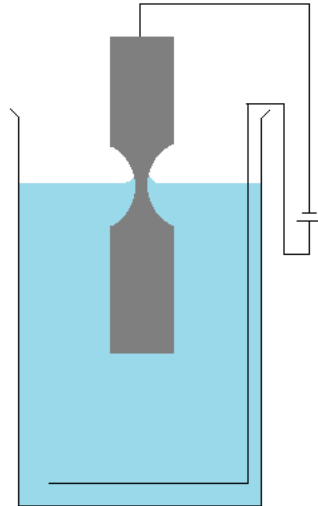
If a negative bias is applied to the tip, there is only small currents from the dopants until the valence band of the tip and the conduction band of the sample aligns, and the negative current increases exponentially, shown at point 1 in figure 7b .

### 3.5 STM tips

The most commonly used metal tips for regular STM measurements is chemically etched tungsten tips. These tips are created by dipping a tungsten wire into a natrium hydroxide (NaOH) solution and applying a voltage. The voltage will make the solution creep up a little along the tungsten wire and the NaOH will start to etch the wire. This will eventually create a neck at the interface with the surface and when the neck is thin enough the weight of the wire

will cause the neck to break. This will consistently create a fine tip with a good aspect ratio and the setup is shown in figure 8.

Similar etching methods are used with other materials as well, like platinum-iridium and more exotic alloys. The common methods for refining tips is either a secondary more complex etching step or milling of the tips with an ion beam or sputtering [23].



*Figure 8. Setup for the chemical etching of tungsten wire in a glass beaker.*

Metal nanowire probes for AFM and STM use have been created by electro depositing a large number of metal nanowires on the top of a metal wire. By using a focused ion beam wires are removed until a single wire is left [8]. With this process nanowire tips of several different metals can be manufactured with high precision. This might be applicable with semiconductor nanowires but it is time consuming and expensive to manufacture a single tip with this approach.

### **3.6 Other microscopy techniques**

#### *2.6.1 SEM*

A Scanning electron microscope accelerates a beam of electrons to an energy in the keV-range and focuses the beam at a point on a sample. When the electrons hit the sample they create several different signals that can be detected individually and analyzed to yield different properties of the sample.

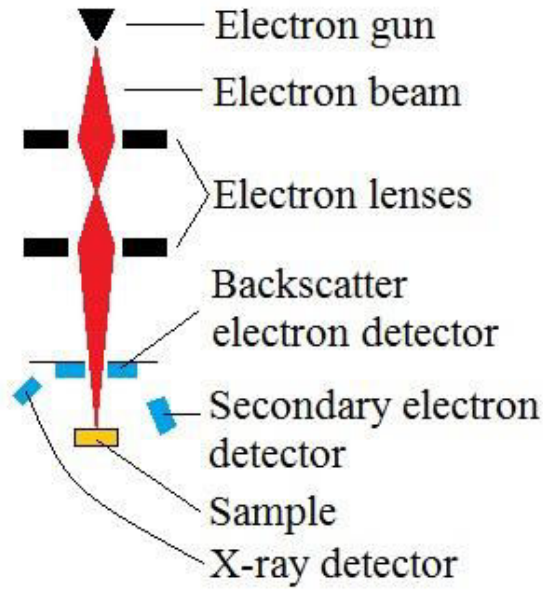


Figure 9. Schematic view of a scanning electron microscope with three different detectors.

When the high energy electrons from the beam interact with electrons of the sample, the interaction might transfer enough energy to local electrons for them to escape the sample. These escaping electrons are called secondary electrons and are detected by applying a positive voltage to a detector close to the sample that attracts the negative electrons. By raster scanning a section of the sample and detecting the amount of and the energy of the secondary electrons emitted at each point, an image of the sample is created. The amount of secondary electrons created by the beam is dependent on the topography of the sample as more electrons can escape the sample from protruding features. This results in the images showing high features as brighter and low features as darker thereby creating a natural topography image.

The secondary electron detector is the most common detector in SEM imaging as it provides both quick and intuitive images. This combined with the high resolution of the SEM made it the preferred examining tool for this project.

### 2.6.2 Optical microscopy

The resolution of optical microscopy is limited by the wavelength of visible light. The rule is that for a structure to be distinguishable from another is that it cannot be smaller than half of the wavelength of the light used in the microscope. The smallest wavelength of visible light is violet light at about 400 nm, which makes features as small as 200 nm distinguishable from each other. There are ways to improve optical microscopy below this threshold and one of these techniques was awarded with the Nobel prize in chemistry in 2014 [24].

For this project the simplicity of imaging in optical microscopy is a positive aspect but the dimensions of the nanowires are close to the visibility limit of regular microscopes.



## 4. Method

The goal of the project is to find an easy and cheap way to glue nanowires to a regular tungsten STM tip. To achieve this several different methods have to be tried and evaluated to reach the optimal process of manufacturing the tips.

### 4.1 Characterizing the nanowires and tungsten tips

The first step in creating nanowire STM tips is characterizing the nanowires by analysis in SEM and optical microscopes. The primary characteristic is their dimensions as they may have a significance in creating the tips.

By using tungsten tips that were not suitable for imaging by themselves we are can get a selection of tip shapes to test which works the best. Therefore the tungsten tips will be characterized in SEM and optical microscopes to examine the topography of the discarded tips and to select those that are to be used. The tips should be clean of contamination and have a single separate surface that could hold the nanowires at the utmost tip.

### 4.2 Creating tips

When creating the tips there are several different variables that have to be tested in the creation process to find the process that yields the best results. The variables tested in this project and the tested modes of these are presented in table 2.

| Length of wires | Tungsten tip shape | Preparation of the wires before application of glue | The glue                   | Glue application               | Method of picking up the wires |
|-----------------|--------------------|---|----------------------------|--------------------------------|--------------------------------|
| 2 $\mu\text{m}$ | Sharp              | Breaking the wires with the tip                     | Indium                     | Dipping by hand                | Dipping by hand                |
| 3 $\mu\text{m}$ | Blunt              | Broken wires transferred to a substrate             | Silver epoxy, Epotek e4110 | Dipping by micro manipulator   | Dipping by micromanipulator    |
|                 |                    | Broken wires on the original substrate              | Carbon fiber epoxy         | Slide through a string of glue | Dragging by hand               |
|                 |                    |   | No glue                    | Application via pipette        | Dragging by micromanipulator   |

Table 2. Variables tested in the tip creation process

Each different configuration of manufacturing was used on a batch of 3 tips to reduce the impact of random influences on the evaluation of the process. The process was performed under an optical microscope at all times to increase precision and control.

The first batch was done with the shorter undoped wires, since if the process was initially successful the undoped wires provide an easier to evaluate result in the STM without dopants complicating the measurements. Blunt tungsten tips were used to increase the chances of picking up wires, which was broken off and transferred to a substrate to further ease the pickup of the wires.

At first indium glue was used, because it has the best conductive properties and was predicted to create the best contact between the wires and the tungsten tip. Since the goal was to have a quick and easy process the tips were initially dipped in glue by hand and then immediately dipped in the broken off wires.

Depending on the results of these initial tips the process was evaluated and one variable at a time was changed to arrive at the final process.

All of the different variables tested presented in table 2 are explained further below.

#### *4.2.1 Length of wires*

At nanometer sizes van der Waals forces give a significant contribution to the total force acting on the wires since the surface area of the wires compared to their weight is very large. The length of the wires could make it more probable that the wires will lay down on the surface of the tip instead of standing up. There is a risk of the wires aggregating into clusters when they are broken off from the substrate. As the length of the wires increases, the surface area increases and this makes aggregation more probable.

#### *4.2.2 Tungsten tip shape*

With the ideal tip having a single nanowire pointing out from the tungsten tip, the shape of the original tungsten tip could change the ease to achieve the ideal tip. If glueing wires proved to be easy, the sharp tip could reduce the amount of wires sticking out. If not the blunt tips could increase the chances of getting at least one wire protruding from the surface.

#### *4.2.3 Preparation of the wires before application of glue*

Depending on the difficulty of breaking the wires on the growth substrate, they may have to be broken off before the wires are to be glued to the tips. Another reason to break them off before picking the wires up is that the method of pressing the tip directly on the wires to break them may force the wires to lay flat on the surface instead of sticking out, which is the desired result.

#### 4.2.4 The glue

The glue is a very important part of the finished tip. It has to be conductive to facilitate the contact between the tungsten tip and the nanowire. Considering the goal of the project the glue also has to be easy to apply to the tungsten tips.

#### 4.2.5 Glue application

The method of application of the glue could have a significant effect on the final product. A thin uniform layer of glue is desired so that the glue does not interfere with the wires. If the layer of glue is thicker than the length of the wires it will decrease the probability of wires extending from the tip.

Dipping will be done by hand or with a micro manipulator, a machine that allows movements with micrometer precision. If dipping in a drop of glue results in excessive amounts of glue on the tip, a thin line of glue could be spread on a glass dish and the tip dragged through the glue line.

#### 4.2.6 Picking up the wires

The main goal with the pickup of the wires is to get a sufficient amount of wires and that some of them are protruding from the surface of the tip. Pickup will be tried by dipping the tip in a straight down and up motion onto the nanowire sample or dragging the tip along the surface of the sample. Both of these methods will be tried by hand and with the micro manipulator.

### 4.3 Characterization of completed tips

Since nanowires usually are at the edge of visibility in conventional light microscopes, the completed tips will primarily be examined with a SEM. If any of the tips shows the desired results the tip will be tested as a STM tip. The first test in the STM is to perform a regular scan on a gold foil sample to be certain that a signal and image can be acquired. The next step is to perform STS to examine if they show the expected results of a metal-on-semiconductor measurement. This should confirm if the scan is conducted with the wires or not, since if the spectroscopy shows metal-on-metal behavior the tip is not working as intended.

## 5. Results and discussion

### 5.1 Tip and nanowire characterization

Two sets of nanowires were grown for this project by Zhaoxia Bi and Jonas Ohlsson at Lund University in a MOVPE system. Both samples consist of GaN nanowires, one with undoped wires and the other sample contain wires with a doping of Si-atoms included in the growth process, resulting in an n-type doping.

The first examination of the wires were done in a SEM to measure their thickness and height, shown in figure 10 and 11.

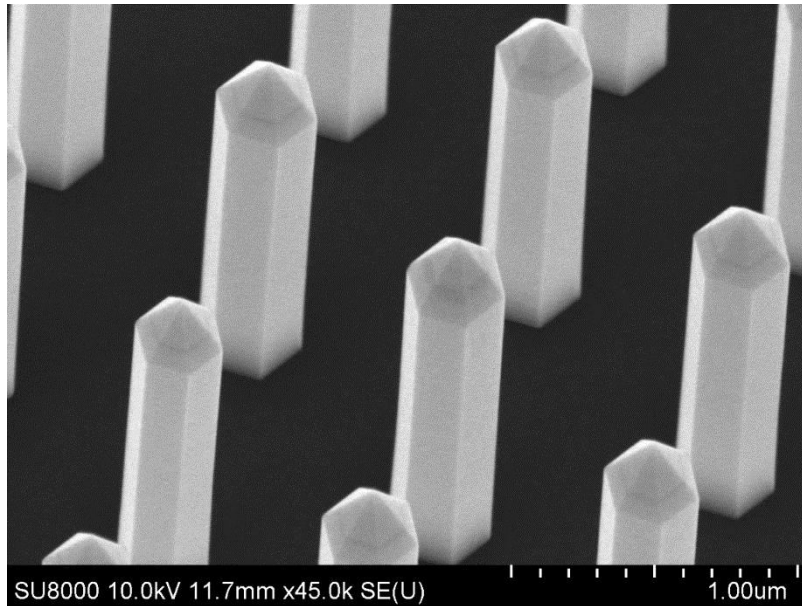


Figure 10. SEM image of the undoped wires used in the project. Taken at a 30 degree angle.

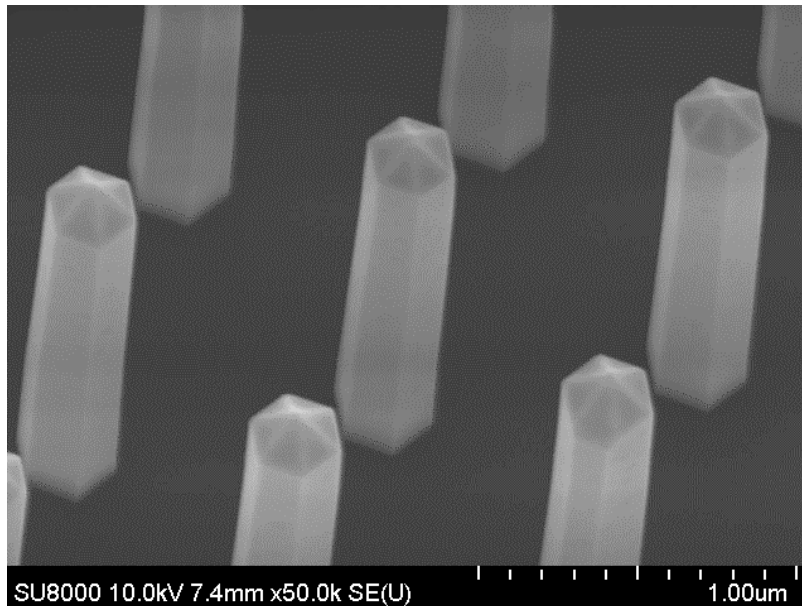
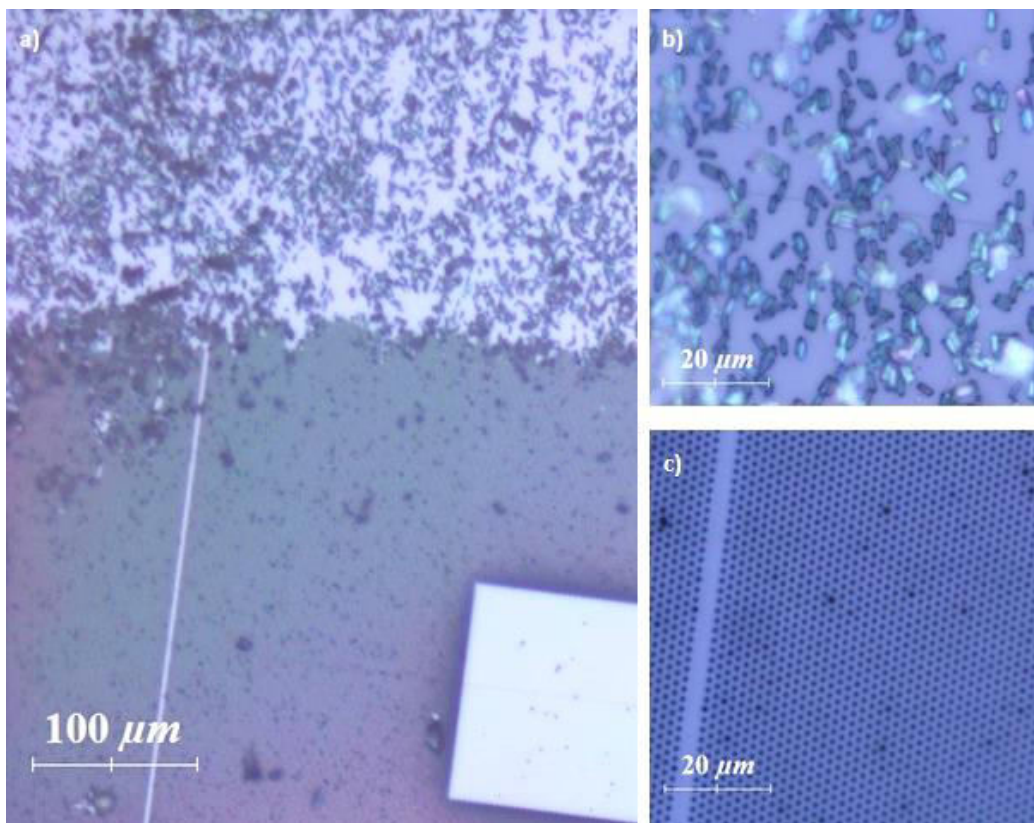


Figure 11. SEM image of the doped wires used in the project. Taken at a 20 degree angle.

Measurements in the images show that the undoped wires have a diameter of about 300 nm and a length of 2 μm. The doped wires have a diameter of about 300 nm and a length of 3 μm. After this some wires were transferred to a silicon wafer by gently rubbing the wafer against an edge of the nanowire sample. This breaks the wires and with the help of van der Waals forces some of the broken wires stick to the silicon wafer. The purpose of the transfer is to test the best method of picking up the wires at a later stage.

After this the wires were examined in an optical microscope, this showed that it is possible to see individual wires with a simple optical microscope, but the low depth of field at higher magnifications is a limiting factor.



*Figure 12. Optical microscopy image of the growth sample after wires have been broken. a) Image of the edge between broken and unbroken wires. b) Broken wires where single nanowires are visible. c) Unbroken wires where the growth pattern is visible.*

An optical microscopy image of a part of the nanowire sample is shown in figure 12a, where the broken off wires can be seen at the top of the image. At the bottom of the image are unbroken wires standing at a perpendicular angle to the microscope. Image 12b shows a closer look at the broken wires and some degree of aggregation of wires can be observed. Pickup of the broken wires should be possible since there still are some present on the sample. Image 12c shows a closer look at the area with unbroken wires. Each dot in the image is a nanowire, and the darker dots are nanowires that are slightly larger than the rest due to imperfections in the growth process.

## **5.2 Creating tips**

During the project some of the variables listed in the method section of this report were ruled out of a possible final process. Because of this all possible configurations of the variables have not been explored. The results presented below are not in chronological order, but rather presented as an evaluation of the different variables in the method chapter. As a starting point

each tungsten tip was cleaned with ethanol and rinsed with deionized water to clean it of contaminants.

### 5.2.1 Length of wires

The size of the wires (2 or 3  $\mu\text{m}$  in length) did not have any significant effect on aggregation of the wires. There were several cases of aggregation with both kind of wires, but this effect seems to be more dependent on the glue. Of the three different glues used here, the silver epoxy was the one who showed significantly more aggregation than the other two. This is probably because it has a low viscosity when applied and has the longest curing time of the three. These two factors could play a major role in allowing the wires to move on the surface and this would increase the chances of them sticking together in clusters by van der Waal forces. A typical case of aggregation is shown in figure 13, where the glue and wires have formed a big cluster which is unusable for further testing.

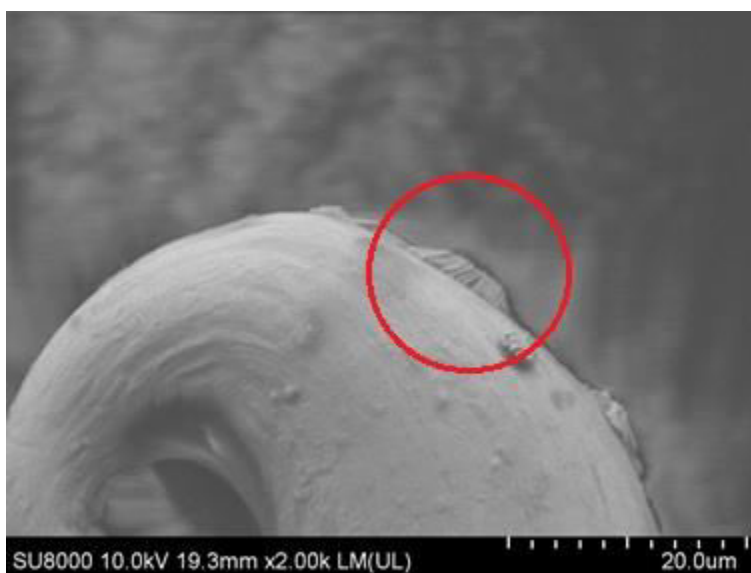


Figure 13. Aggregated doped wires on the surface of a tungsten tip.

### 5.2.2 Tungsten tip shape

Tungsten tip shape played some role in successfully acquiring nanowires at the utmost point of the tips. The best results were from tips that were relatively flat at the utmost point, which made it more probable to have nanowires sticking out at the correct point. Tips that were rounder or sharp showed difficulty in getting wires to stick out that would not get shielded by the tungsten tip itself. An ideal tip shape with a flat surface at the top of the tip is shown in figure 14.

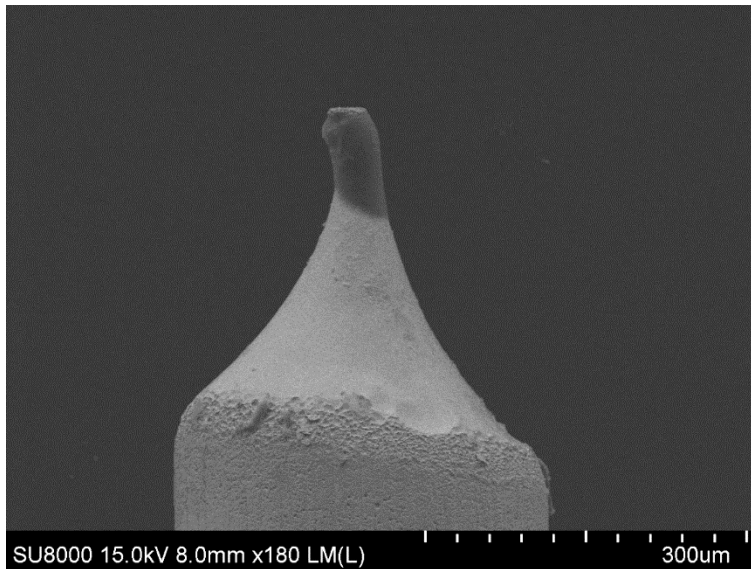


Figure 14. Ideal tungsten tip shape.

### 5.2.3 Preparation of the wires before application of glue

Picking up wires that had previously been broken off and transferred to a substrate was quickly ruled out as a manufacturing method since none of the first three tips created this way had any wires present on them. This was probably because the low amount of wires transferred to the substrate compared to the amount of wires on the growth sample, and the wires may stick to the substrate surface when broken off.

Picking up the previously broken off wires from the growth sample proved more successful, but the broken off wires showed a lot of aggregation as seen in the optical microscope in image 12b and also at further inspection in the SEM as shown in figure 15.

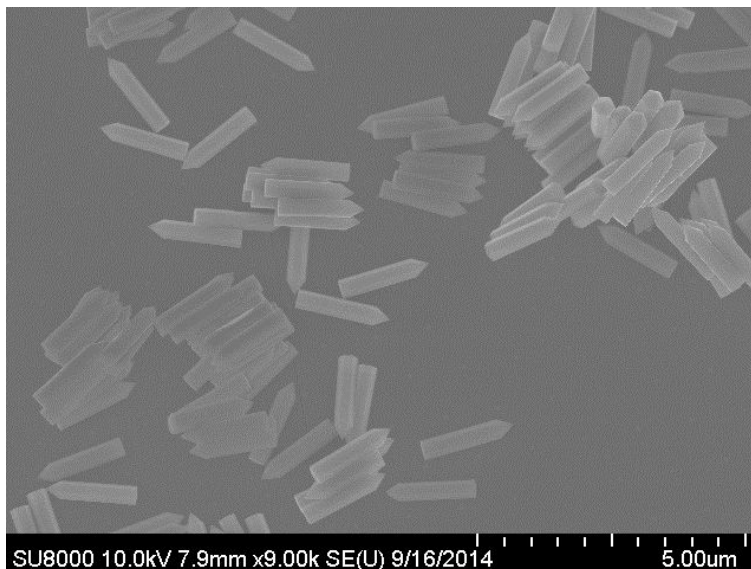


Figure 15. SEM image of broken wires that have formed aggregates on the growth sample.

There were no difficulty in breaking off the wires with the tip directly without prior preparation and the amount of wires picked up was the highest of the three methods. The majority of the wires were laying down on the surface of the tip but there was still enough wires sticking out from the surface to allow testing in the STM. Because of these reasons this was the preferred method and the majority of the tips created were done by dipping the tip directly onto the wires.

#### 5.2.4 The glue

Of all the variables, the glue was the one that had the largest influence on the final product and was the factor that varied the most between individual tips. The first tips done without glue had no wires present so this possibility was not examined further.

The indium glue had to be melted before application to the tip and this became a problem as the indium solidified too quickly when applied to the tungsten tips. As a side effect of this it was difficult to get a uniform thin layer of indium on the tips. The molten indium stuck to the surface of the tungsten tips and solidified partially, which resulted in a large amount of malleable indium sticking to the tip and making it impossible to pick up wires before the indium solidified completely.

To solve this problem the indium, with a melting point of 156° C, was heated to 300° C on a hot plate before the tip was dipped in the glue and then quickly dipped in the wires before the indium solidified. The results from this process varied greatly, the first tip created with this process was a success with wires sticking out from the surface, shown in image 16. But this result could not be replicated and the other tips created with this glue showed lots of wires, but few protruding from the surface, a typical example of this is shown in image 17.

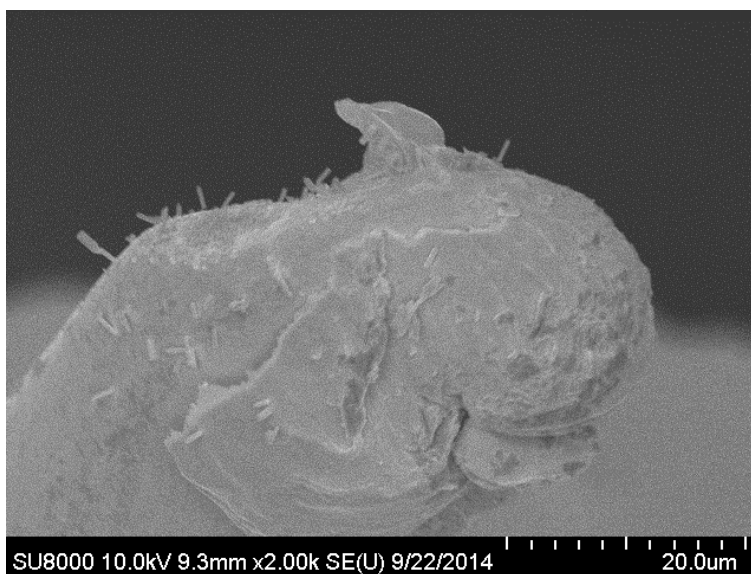


Figure 16. Successful tip with undoped wires and indium glue.



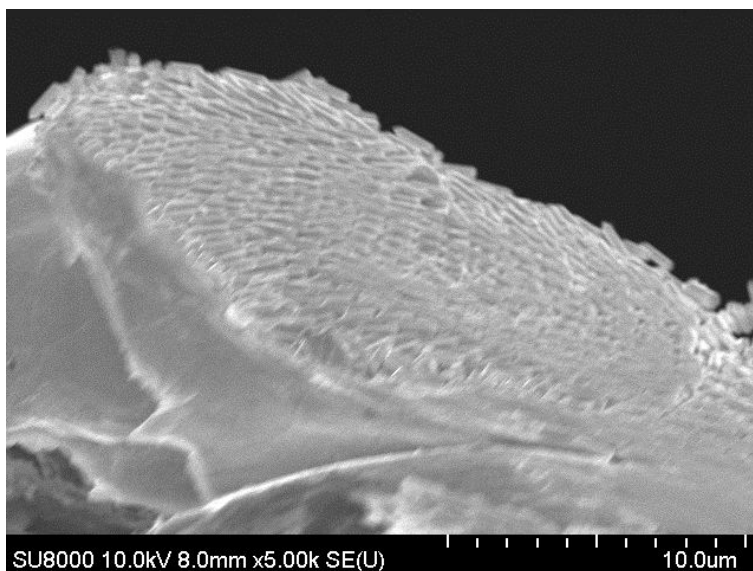


Figure 17. Wires on the surface of a tip with indium glue.

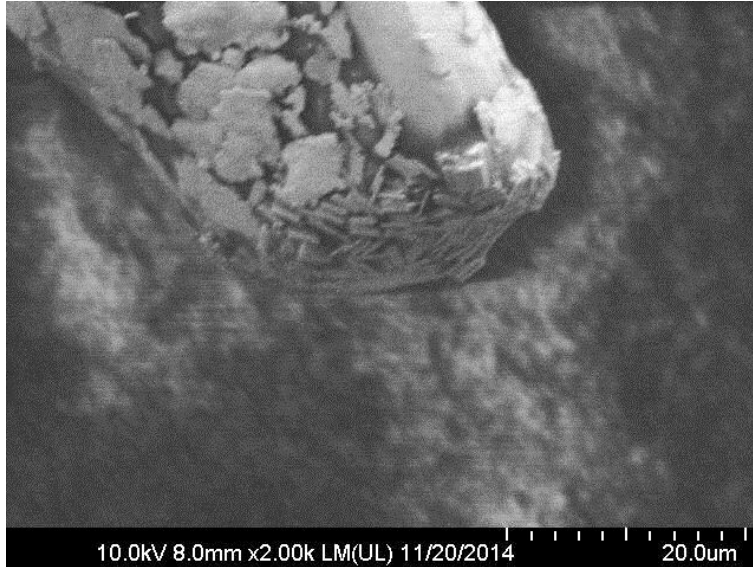
There were some problems with the silver epoxy as well. The two components of the epoxy were both rather old and the silver particles had formed large flakes. These flakes were several times larger than the nanowires and this became a problem as the flakes could extend beyond the nanowire height, as shown in figure 18. But as one of the first tips created with this glue had protruding nanowires, we continued using the silver epoxy to replicate the result.



Figure 18. Tip with silver epoxy and clear silver flakes present on the tip. The red circle shows a silver flake extending from the surface.

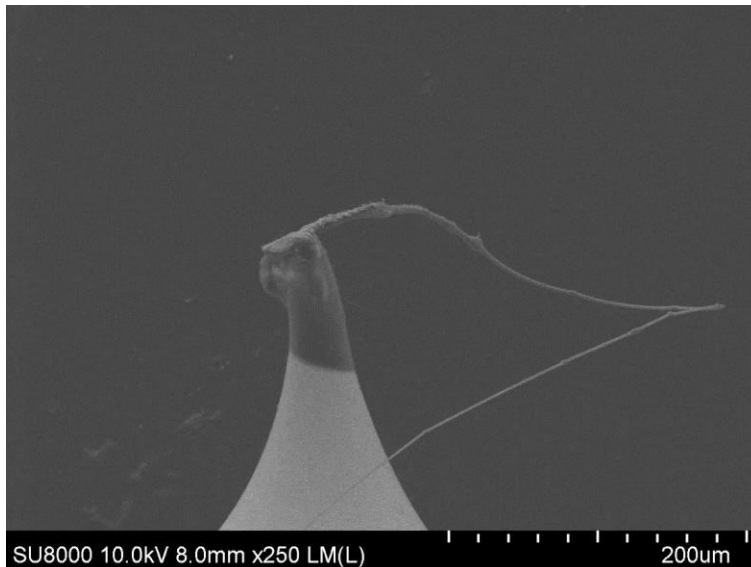
In contrast to the indium glue, the silver epoxy had a low viscosity and a long curing time which made it much easier to apply the glue and pick up the wires. The long curing time and low viscosity allowed the wires to move more and as previously mentioned this caused a lot of aggregation of the wires. The increased mobility of the wires also seem to prevent any wires

being left sticking out of the surface. Of all the manufacturing processes tested with the silver epoxy, none had the desired results. All tips with silver epoxy had wires at the tip and if the process could be altered to get a few wires in the correct position the silver epoxy might prove to be a good alternative.



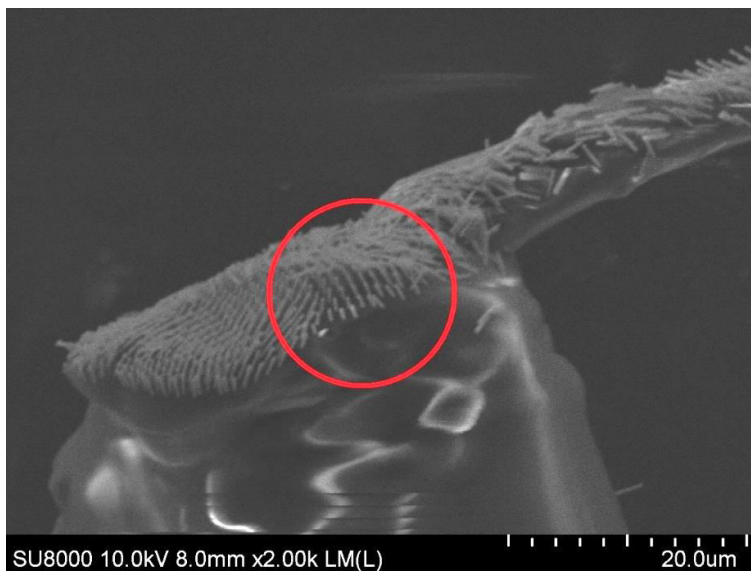
*Figure 19. Tip created with silver epoxy, showing a lot of wires at the utmost tip, but none extending beyond the surface.*

The carbon glue provided the best results of the three glues. It has a curing time of about 20 minutes and a low viscosity. This made it easy to apply to the tip and created a uniform layer, as seen in image 20, where the dark area of the tip has been dipped in the carbon glue. A short curing time provided some problems as well, if the glue was allowed to cure a little before the tip was dipped in it, strings of glue often formed when the tip was pulled out, shown in figure 20. These strings made STM measurements impossible so a quick application of the glue and pickup of the wires is preferred.



*Figure 20. Tip with a string formed by dipping in partially cured carbon epoxy.*

Pickup with the carbon glue proved to be very effective, and in some of the tips the wires were picked up standing in the growth pattern from the sample. This effect can be seen in figure 21, which is a closer view of the tip in figure 20.

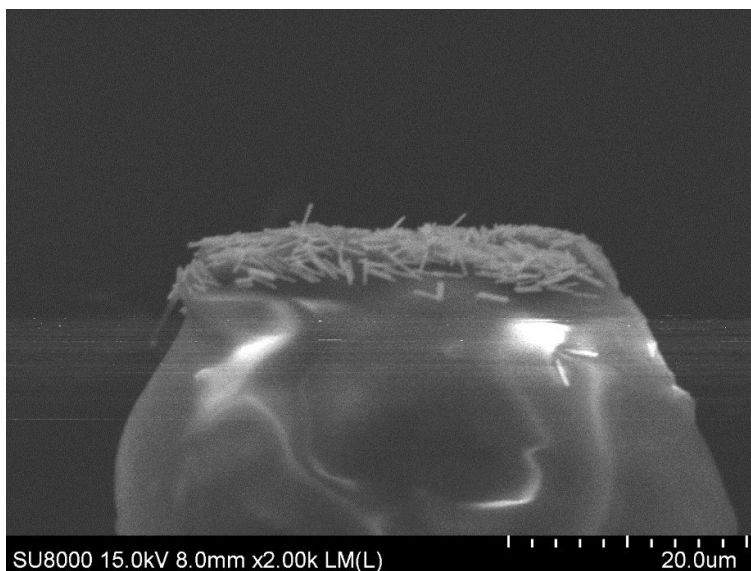


*Figure 21. Tip with carbon glue and doped nanowires. Red circle showing that the wires have been picked up in the pattern they were grown in.*

When the tips with carbon glue were examined in the SEM, live movement of the wires could be observed. This is probably caused by the high energy electrons from the electron beam melting the glue, which allows them to move. Charge buildup in the wires may be a contributing factor to the melting of the glue, and this may be a sign of a bad contact between

the nanowires and tungsten tip. After this effect was observed the time each tip spent in the SEM beam was minimized to keep the impact as low as possible.

All of the tips created with the carbon glue consistently had wires sticking out and some of them were close to the ideal tip. A closer look at the tip in image 20 shows such a result, in figure 22.



*Figure 22. Magnified tip from figure 14 with carbon glue and a few wires sticking out.*

### *5.2.5 Glue application*

The effectiveness of the different glue application methods depended on the glue. Since the indium glue had to be melted this ruled out using pipettes and the micro manipulator for dipping. The melting also made it very difficult to create a thin enough string of the glue to make dragging a good option. Because of this all of the indium tips were created by dipping the tip in the glue by hand.

The low viscosity of the silver epoxy allowed for testing of all the methods listed. There were no visible differences from these methods as the glue layer on all the tips appeared similar. When preparing the carbon glue tips the low curing time was a similar problem to the indium glue. During the preparations the glue partially cured and carbon glue strings were formed when the tip was pulled out of the glue, as shown in figure 20.

### *5.2.6 Picking up the wires*

Due to the limitations of the glues in regard to the short curing time the main method for fabrication was dipping by hand for both indium and carbon glue tips.

The results with the silver glue showed that the increased precision of the micro manipulator improved the amount of wires picked up and the positioning of the wires on the tip. Dragging the tip on the sample only improved the amount of wires on the sides of the tip, so dragging was only used for a few of the tip processes.

Presented below is table 2 with each square colored to represent the test results presented above.

| Length of wires | Tungsten tip shape | Preparation of the wires before application of glue | The glue                   | Glue application               | Method of picking up the wires |
|-----------------|--------------------|---|----------------------------|--------------------------------|--------------------------------|
| 200 nm          | Sharp              | Breaking the wires with the tip                     | Indium                     | Dipping by hand                | Dipping by hand                |
| 300 nm          | Blunt              | Broken wires transferred to a substrate             | Silver epoxy, Epotek e4110 | Dipping by micro manipulator   | Dipping by micromanipulator    |
|                 |                    | Broken wires on the original substrate              | Carbon fiber epoxy         | Slide through a string of glue | Dragging by hand               |
|                 |                    |   | No glue                    | Application via pipette        | Dragging by micromanipulator   |

*Table 3. Tested variables, color coded to show results of testing. Green for successful, yellow for inconclusive and red for unsuccessful.*

### 5.3 STM and STS measurements

Of the tips created during this project, measurements in the STM was performed with the tip shown in figure 16. The scans were performed on a gold foil at a positive bias of 5V to the tip, to be certain that the scan is done outside of the band gap of 3.39 eV of the GaN nanowires.

The first images taken with the tip did not provide images of good quality, as shown in figure 23a-b. Scanning is done horizontally and the measured signal appears to continue after the feature circled in image 23a resulting in a smeared look. The images still give some information on the topology of the sample and the encircled detail could be a step between atomic planes.

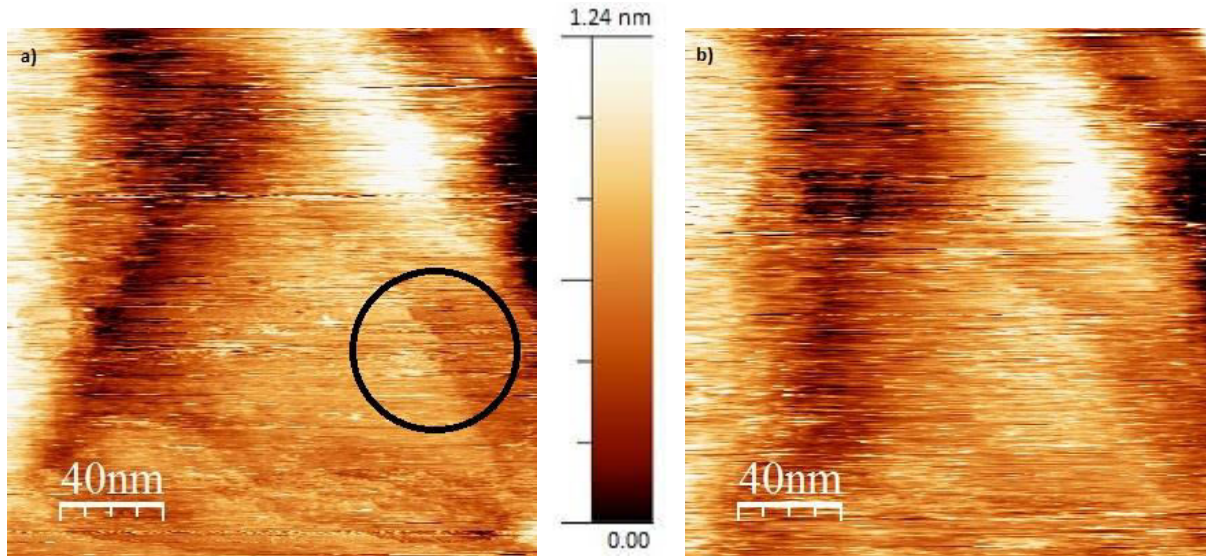


Figure 23a-b. Forward and backward STM images taken with a nanowire tip.

Several spectroscopy measurements were performed during repeated scanning of the sample showing a promising I-V curve.

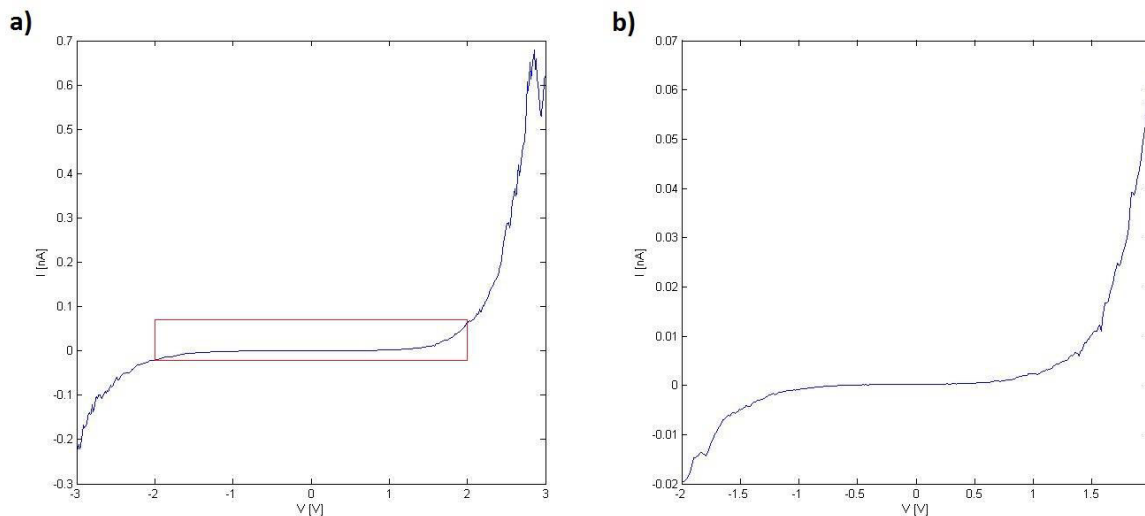


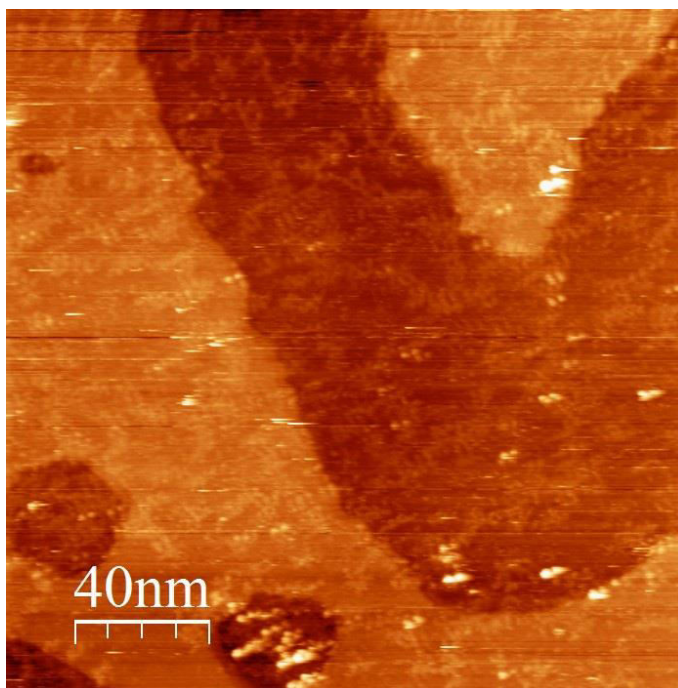
Figure 24a-b. a) I-V curve of STS measurement with a nanowire tip on gold foil. b) Closer view of measurements between -2 and +2 volts marked with red square in a)

The spectroscopy was performed with an interval from -3V to +3V, and showed the predicted shape of the curve if scanning is done on a metal with a semiconductor tip. A band gap of 3-4V can be seen, as the difference in current between -2V and +2V is approximately 80 pA. This is close to the expected 3.4V band gap of undoped GaN when accounting for band broadening effects. The settings were altered a little between each spectroscopy measurement to test the effects on the tip and an additional four of the measurements are presented in the appendix.



After 20 spectroscopy measurements, the scanning image became clear and a good image quality was achieved as seen in figure 25. These images also showed clear signs of ghosting as all major structures has an identical twin next to it.

Spectroscopy after the image quality improved did not have the semiconductor characteristic and instead showed metallic behavior. All of this is consistent with measurements using a normal tungsten tip on a metal. This was also done during the project for comparison (not shown).



*Figure 25. STM image with clear signs of ghosting, since all features appear twice.*

To examine what had happened to the tip it was removed from the STM and then examined in a SEM which showed that there were no wires present on the tip. It appears that the spectroscopy measurements is close enough to the pulsing technique used in the STM for cleaning oxides off of tungsten tips that the wires have been pulsed off. A cleaning pulse is usually performed by applying a quick voltage change on the tip while it is conducting a current. In future testing the time between each step in the STS measurement may have to be increased to mitigate this problem.

If the wires had been removed by the tip accidentally crashing into the sample some of the wires should still have been present when examined in the SEM.

## **6. Conclusion and outlook**

The first goal of this project was to find a quick and easy way to create STM tips with a nanowire as the scanning medium. With the results presented in this report it has been shown that it is possible to create such tips with more than one method and that there still is several points that might improve the manufacturing method. The tip shown in image 22 took 15

minutes to create and another 30 minutes of evaluation in the SEM. The final process for creating these tips was:

1. Examine the tungsten tip with an optical microscope
2. Clean the tungsten tip with ethanol followed by deionized water
3. Place nanowire sample in the optical microscope
4. Place one drop of the carbon glue on a glass dish
5. Pick up the tungsten tip with tweezers and dip it into the glue
6. Dip the tungsten tip in the nanowire sample at a 90 degree angle to the sample
7. Let the tip cure fully before inserting it in the SEM for examination

With this process one of the three tips tested showed the desired result while two had long carbon strings from partly cured glue hindering use in the STM as seen in image 11. Nanowires sticking out was present on all of them so the yield can be significantly improved if the formation of strings can be minimized. With the manufacturing process with the carbon glue showing good signs of producing usable tips the continuation of the project should focus on improving imaging in the STM. Since the major factor in producing good tips appeared to be the glue, other glues than the three tested here may also be explored to improve the tip quality.

Imaging in the STM with the tips was only partly successful as imaging was possible but the resulting images were not of good enough quality. With further work on the settings in the STM with the nanowire tips the imaging quality should be improved.

If it proves impossible to achieve imaging with the tips created in this project, it may still be a viable way to perform I-V measurements on single nanowires.



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## 8. Appendix A. Spectroscopy measurements

