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Nanowire analysis by Atom Probe Tomography

Barrois, R.

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Nanowire Analysis by Atom Probe Tomography

Rion Barrois

21-07-2014

Summary

Atom probe tomography (APT) is used to analyze the structure and chemical composition of a material on an atomic scale. Therefor, the atom probe uses an electric field and a laser to sequentially evaporate single ions from a tip-shaped specimen and projects them onto a detector. After the ions are evaporated, their chemical identity and original position can be determined from their time-of-flight, sequence of arrival and the position at which the ion hits the detector. This makes it possible to reconstruct the original specimen atom by atom.

The aim of this project is to prepare samples of nanowires for atom probe analysis, in such a way that the measurement can be done directly on the substrate on which the nanowires were grown. While doing so, the main problem is that nanowires are usually grown relatively close together, which makes it impossible for the atom probe to evaporate atoms from only one nanowire. However, for a useful atom probe analysis, it's absolutely necessary that all detected atoms are coming from a single tip. Hence, a single nanowire has to be isolated on the substrate.

In order to prepare a nanowire sample for APT, we developed a procedure existing of three steps. During the first step, a mask (with holes in it) is pressed against the sample with nanowires. By doing so, all wires that don't go through one of the holes, are removed from the substrate or pressed down upon the substrate, thus creating isolated patches of nanowires. During the second step, the focused ion beam (FIB) is used to remove all standing wires in those patches, only one wire is left standing. The third step is necessary to clean the substrate from all wires the were pressed down during the initial step.

This procedure has resulted in some well-isolated nanowires that could be used for APT. Nevertheless, the method still needs to be improved to achieve reproducible results. Furthermore, we found that the success of APT-analysis depends mainly on the used sample and not on the isolation procedure.

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1 Introduction

During his famous '*There's plenty of room at the bottom'*-lecture in 1959, Richard Feynman discussed the idea of implementing technology on extremely small length scales. He talked about the possibilities of manipulating matter on molecular and atomic scales, building structures atom by atom, and designing nanoscale computing machines and other nanodevices [1].

Now, 55 years after Feynman's lecture, nanotechnology has a lot of modern day application. Nanostructures are, for example, implemented as components in commonly used electronic devices, such as phones and computers. Due to nanotechnology, the sizes of these devices have decreased enormously the past couple of decades, while their capabilities have increased. To continue this general trend of minimization in the world of electronics, researchers are continuously trying to create new nanomaterials or to improve the old ones.

Designing and optimizing new materials to fulfill a given function usually requires an in depth understanding of the material properties and their relation to the materials atomic structure. When investigating these relations, it's important to have tools that are able to characterize the structure and composition of these materials. For extremely small nanostructures, the traditional optical microscope is generally not sufficient. It is therefore necessary to use alternative techniques, such as electron microscopy or atom probe tomography (APT). In contrast to optical microscopy, both of these methods are capable of looking at objects smaller than the wavelengths of visible light [2].

APT uses a high electric field (in combination with a laser) to evaporate ions from the top of a tip-shaped specimen. After the ions are released from the surface of the tip, they are accelerated towards a detector, which allows to determine the original position of these atoms within the specimen and their mass-to-charge ratio, which corresponds to the elemental nature of the evaporated atoms. By combining this information, it's possible to reconstruct a 3D model of the original specimen, providing atomic scale information of the structure and the composition of the sample [3]. In chapter 2 the principle of APT will be discussed in more detail.

During this project, we aim to analyze nanowires with APT. Nanowires are cylindrical nanostructures with diameters in the orders of few tenths or hundreds of nanometers and are usually grown in dense arrays on wafer-like substrates. However, to make an accurate APT-analysis of a nanowire, ions from only one single nanowire have to be evaporated at a time and hence the nanowire has to be isolated from all the others. Therefore preparing appropriate samples is very important for a successful APT-measurement.

The aim of this project is to develop a preparation procedure, which prepares a nanowire sample for atom probe analysis in such a way that the measurement can take place directly upon the substrate where the nanowires were originally grown on. The main goal of this procedure should be to make sure that all evaporated atoms are coming from one single nanowire by removing all other wires in the surroundings. Especially the possibility of using a mask to press standing nanowires down to isolate a single wire, is investigated.

2 Theory

2.1 Nanowires and their applications

During the '*There's plenty of room at the bottom'*-lecture, Richard Feynman talked about the development of nanotechnology and nanodevices. He proposed to make these devices out of very small components, which should be connected to each other by very tiny wires: nanowires [1]. These wire-like structures, with diameters in the order of nanometers, are crucial to build nanodevices, because they are responsible for transporting electrical currents or photons and thus information within the device.

Since *There's plenty of room at the bottom*, a huge variety of different nanowires have been developed: metallic and semiconducting types as well as organic ones. All of these are created out of different chemical compounds and have different structures and geometries and consequently also different optical, electrical and magnetic properties. Moreover, it's possible to stack different layers on top of each other to grow a nanowire or to dope nanowires with a controlled amount of dopants [4].

Because of their versatility, nanowires can be used in lots of different applications. Nanosized p-n junctions (created by doping a nanowire) are, for instance, used as transistors in electrical circuits [5]. In solar cells the same structures are used to absorb sunlight and convert the absorbed photons into an electrical current [4]. Nanowire crossings can act as logic gates and can therefore be used to build small computing devices [6] and nanowires can even be used for medical purposes, as parts of biosensors [7].

2.2 The growth of Nanowires

Nanowires can be grown in a number of different ways. It is possible to distinguish between top-down and bottom-up approaches. The top-down approach starts with a big piece of material and reduces it to a substrate with nanowires on top by, e.g., lithographic techniques. The bottom-up approach starts with an empty substrate and grows the nanowires on top of the surface by continuously adding the growth compounds.

All of the nanowire samples that are used during this project are grown by a bottom-up technique which is called Vapor Liquid Solid-growth (or VLS-growth). To grow nanowires using this method, gold droplets are placed upon a substrate, for example, by reducing a full gold layer to droplets. These liquid gold droplets act as catalyst for the growth process by absorbing vapor from their surroundings, forming a liquid alloy. After the liquid alloy gets supersaturated, the absorbed vapor starts to cluster together within the alloy droplet, forming a solid nanowire underneath the droplet [8]. Figure 1 schematically shows how the VLS-process works.

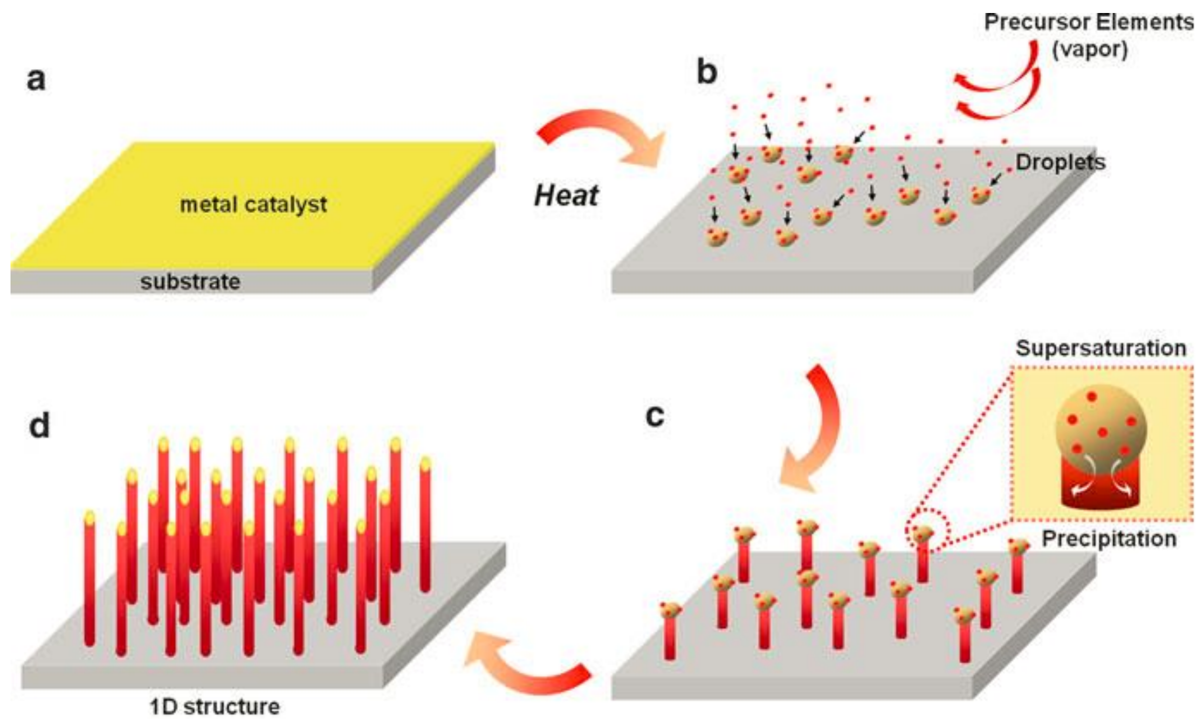

Figure 1:A schematic overview that explains the Vapor Liquid Solid-growth process [8].

How the grown nanowire sample eventually looks like, is determined by the position and diameter of the gold droplets that are placed upon the substrate. There are a number of different ways to control the gold deposition. It is, for example, possible to use Electron Beam Lithography (EBL) to reduce a complete gold layer into small droplets with a chosen position and diameter [9]. Figure 2 shows this method in more detail.

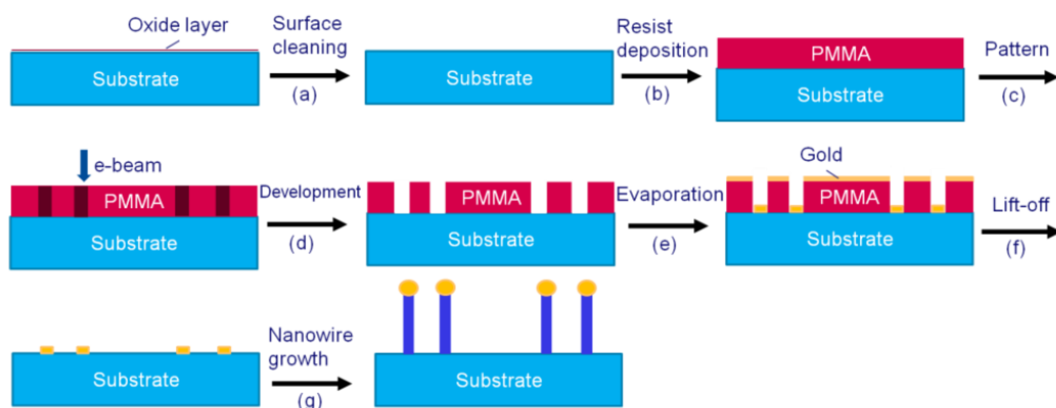

Figure 2: A Schematic overview that shows the EBL-method for controlling the deposition of gold droplets on the substrate [9].

A second method to control the deposition of gold droplets, is called nanoimprint lithography (see figure 3 below). This method uses a stamp to create a pattern of mechanical deformations in which the gold is deposited. The results of this method are similar to the results of the EBL-method, but they are achieved at a considerably

lower cost. Another advantage of this method is that it can be used to produce a larger quantity at once [9].

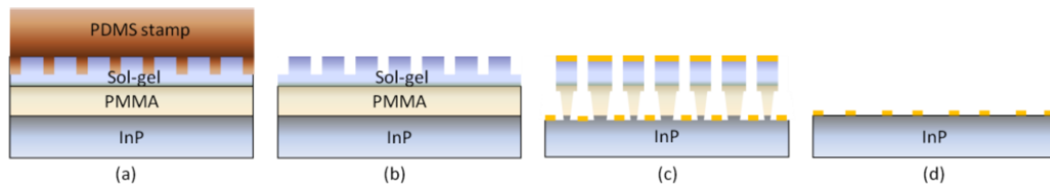

Figure 3: A Schematic overview that explains the gold deposition by nanoimprint lithography [9].

A third way to deposit gold droplets on top of a substrate, uses a so-called 'colloid', which are gold nanoparticles in a liquid medium. This colloid is deposited on the surface of the substrate. After the deposition, the liquid medium is removed, only leaving the gold particles on the substrate. The disadvantage of this method is that the exact position of the gold droplets, and thus the nanowires, cannot be controlled. Consequently, these samples are very irregular. However, the density of nanowires on the substrate and the diameter of the grown nanowires are determined by the properties of the used colloid and can thus be controlled [10].

2.3 The basics of atom probe tomography

Since the size of a nanowire is usually comparable to or smaller than the wavelengths of visible light, traditional optical microscopic techniques are generally not sufficient to characterize nanowires. Other methods, such as electron microscopy (SEM/TEM) and atom probe tomography (APT), provide better results. During this project electron microscopy is used to look at the samples that are prepared for atom probe analysis. In order to understand how the sample should be prepared, however, it's important to know the basics of APT, which will be discussed in the remainder of this chapter.

Atom probe tomography relies on the evaporation and characterization of individual atoms from the top of a tip-shaped specimen. Evaporation can only occur when the energy of an atom exceeds the energy of the local bonding between the atom and the surface of the specimen. There are two ways to control this evaporation during an APT-measurement: raising the temperature of the specimen increases the kinetic energy of the atoms and thus the possibility of evaporation, applying an external electric field increases the potential energy of the atoms and thus also the possibility of evaporation. By choosing a right combination of temperature and electric field, the evaporation of ions from the specimen surface can be controlled (see figure 4).

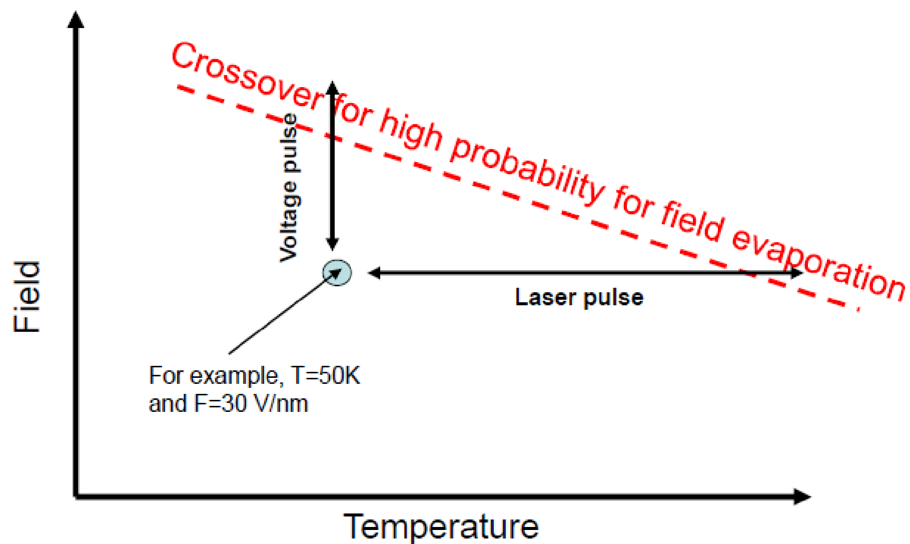

Figure 4: A graph illustrating how the evaporation of atoms during an APT-measurement depends on the temperature and the electric field [11].

However, since APT is not capable of evaluating a continuous flow of evaporated ions, a pulse-triggered evaporation is required for a successful APT-measurement. The combination of temperature and electric field is, therefore, chosen in such a way that the energy of the atoms is just below the threshold energy for evaporation. By periodically increasing the electric field or the temperature (pulsing) in such a way that only the extra energy pulse triggers the evaporation of atoms, it is possible to control the timing and amount of the evaporation events precisely. Paragraph 2.5 deals with these pulsing modes in more detail.

2.4 The atom probe setup

An atom-probe setup is an ultra-high vacuum (UHV) system. As most commercial UHV-systems, it consists of three vacuum chambers: the load lock chamber, the buffer chamber and the analysis chamber. Figure 5 schematically shows the analysis chamber in which the actual APT-measurement takes place.

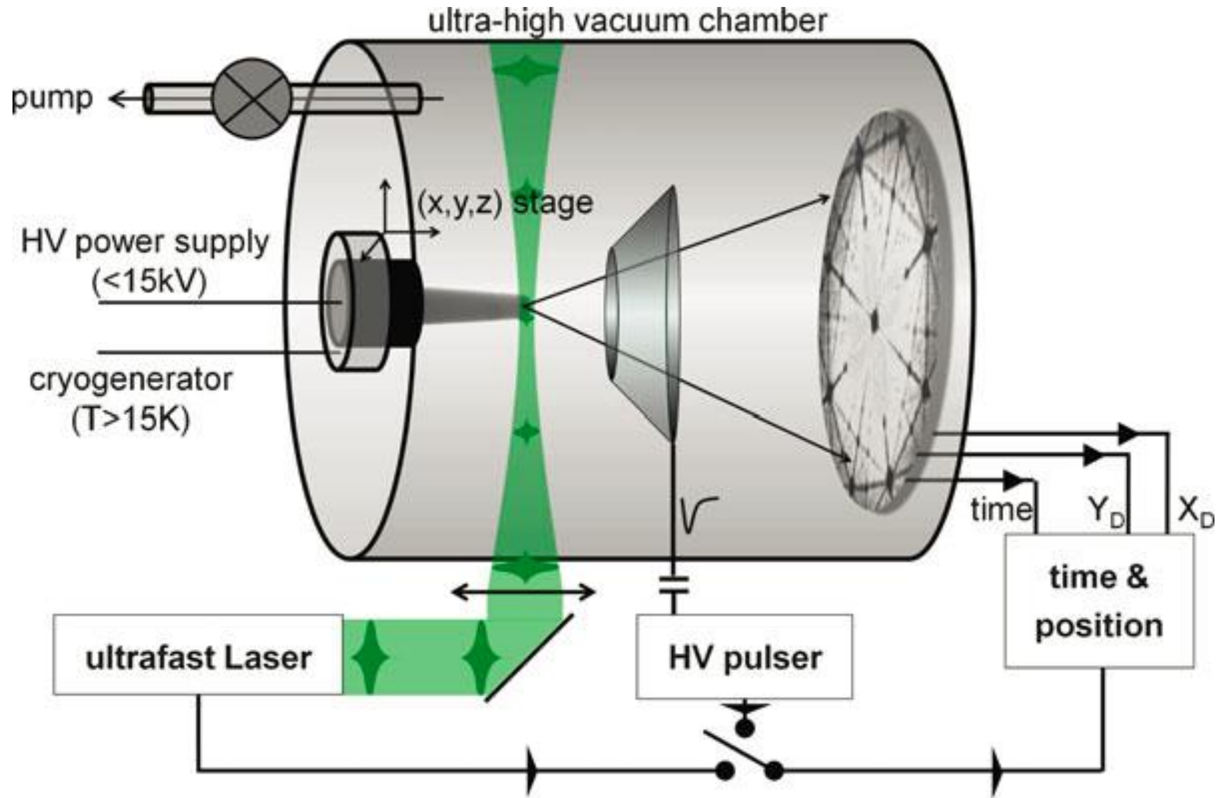

Figure 5: A schematic overview of the analysis chamber of an atom probe [3].

The temperature and the pressure within this analysis chamber are continuously controlled by a vacuum pump and a cryohead. When a specimen is loaded from the buffer chamber into the analysis chamber, it's mounted on a movable stage. A DC, high-voltage power supply is connected to this stage to generate the required electrostatic field. By moving the stage, the tip of the specimen is aligned with the local electrode (for high-voltage pulsing) or with the laser (for laser pulsing). Both pulsing techniques will be further discussed in the next paragraph.

While an ion is evaporated from the surface, one of its electrons is drained into the surface, ionizing the atom during the process. The created ion is accelerated towards micro channel plates by the external applied electric field. When an ion enters these plates, it causes the release of a cloud of electrons which is also accelerated by another electric field. This electron cloud hits a delay line detector which records its position of impact, while the time between the pulse (that has triggered the field evaporation) and the moment of impact on the detector is measured [3].

The measured time of flight is directly related to the kinetic energy of the evaporated ions, and can be used to determine their mass-to-charge ratio. The relation between the time of flight and the mass-to-charge ratio is given by the following expression:

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{d_{detector}}{t_{flight}}\right)^2 = neV \tag{1}$$

$$\frac{m}{n} = \frac{2eVt^2}{d^2} \tag{2}$$

The mass-to-charge ratio of an ion can be related to its chemical identity. So, by measuring the time-of-flight of each detected ion, it’s possible to identify the chemical composition of the specimen.

Combining this chemical information with the data from the delay line detector (corresponding with the x- and y-coordinates of the atom in the original specimen) and the detection sequence (corresponding with the z-coordinate), makes it possible to reconstruct a 3D-model of the original specimen, providing atomic scale information about the structure and composition of the sample [12].

2.5 Controlled field evaporation

The previous paragraphs described the principle of field evaporation and how it is used during an atom probe tomography measurement. These paragraphs also discussed the importance of a pulsed triggering of the evaporation process: an atom probe is best at analyzing atoms one at a time and it most of the time cannot work with a continuous flow of evaporating atoms.

The first atom probes were only equipped with a voltage pulsing technique to control the evaporation. Currently, however, atom probes can be operated in voltage pulsing mode as well as in laser pulsing mode. Which method should be preferred, strongly depends on the experiment. This paragraph will discuss both pulsing techniques and compare them.

2.5.1 High voltage pulsing

High voltage pulsing periodically increases the external applied electric field to trigger the evaporation of atoms. The application of this method is primarily limited to metals, since it requires the material to have a sufficient high electrical conductivity and semiconducting and insulating materials in general do not satisfy this requirement.

While voltage pulsing, nearly all ions are released at the maximum of the pulse, which is in agreement with the figure shown below.

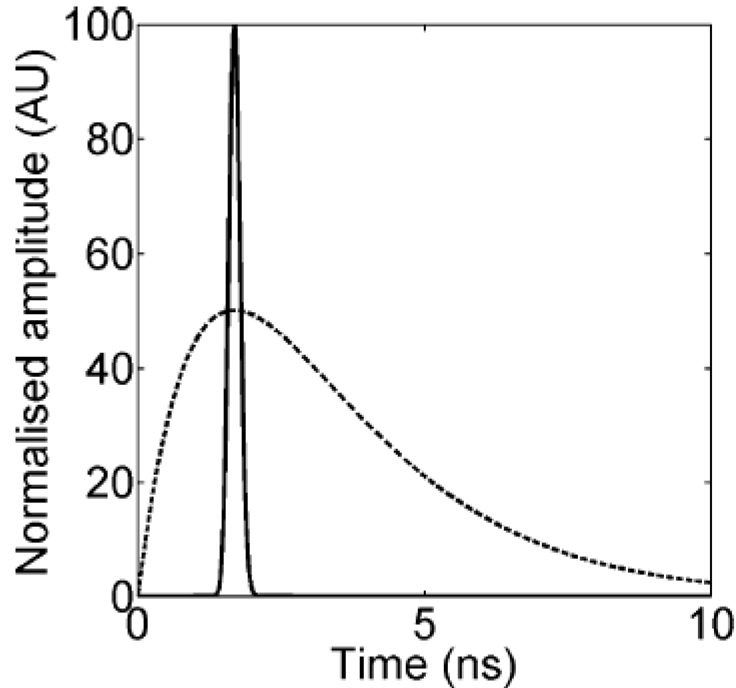

Figure 6: A graph showing the correlation between the high-voltage pulse (dashed line) and the probability of field evaporation (solid line) [3].

Figure 6 clearly shows that there is a small timespan in which ions evaporate. Since the electric field (pulse) changes during this period of time, this means that the released ions can have different kinetic energies. These small variations in energy result in small mass deficits of the detected ions and consequently in a reduced mass resolution. The introduction of the reflectron within the atom probe, however, partially compensates for the spread in energy by increasing the distance between the tip of the sample and the detector.

Another important disadvantage of voltage pulsing is that this method exposes the specimen to a periodic stress, which will eventually fracture the sample (while maybe damaging the local electrode during the process) [3].

2.5.2 Laser pulsing

Laser pulsing periodically triggers field evaporation by increasing the temperature of the sample. By focusing the laser on the tip of the specimen and locally increasing the temperature there, the atoms at that specific place within the sample will have a larger kinetic energy, which makes it easier for them to escape from the surface of the specimen.

Since laser pulses can be extremely short (compared to the voltage pulses in figure 6), the laser pulsing method has a better mass resolution, because it doesn't experience the same energy deficits as voltage pulsing. It also has a better signal to noise ratio (less background) and doesn't cause any stress within the material.

However, the extra kinetic energy may cause the atoms to move over the surface of the material and will certainly cause deviations in the flight path of the evaporated ions. When laser pulsing too fast, the tip could also become over-heated. All three of these effects decrease the spatial resolution of the 3D reconstruction [13]. Because of these disadvantages, voltage pulsing is most of the time preferred above laser pulsing.

3 Isolating a single nanowire

3.1 Introduction

Nanowires are usually grown in large and dense arrays. However, to analyze nanowires from a specific sample by atom probe tomography, one single nanowire needs to be isolated from all other standing wires within a radius of a few hundred micrometer. This is to make sure that all detected ions are coming from the same tip, which is necessary for the 3D reconstruction. If the sample isn't prepared in this way, the atom probe will evaporate atoms from different wires during a single measurement. When the sample is reconstructed afterwards, all the measured ions will be formed into one single tip, which was obviously not the case.

There are quite a few different techniques that could be used to isolate wires upon a substrate. A few of these methods will be discussed in this chapter.

3.2 Growing nanowires further apart.

The easiest way to obtain an isolated nanowire is, obviously, by growing only one single nanowire on a substrate (a very sparse array of wires would do as well). In principle, this can easily be done by the VLS-growth method described in paragraph 2.2.

Most of the time, however, atom probe tomography should be used to analyze nanowires that are grown for specific applications and these samples aren't especially prepared for APT. So, unless it is possible to recreate one of these wires exactly and on an individual basis, it's not possible to analyze these kind of samples using this method.

Unfortunately, it's in general not possible to do this, because the wire-to-wire spacing influences the growth process and thus the properties of the grown wires. Especially the growth rate is depending heavily on the interspacing between the wires. This dependence is caused by differences in absorption of vapor (which fuels the growth of the nanowires) for different wire densities. When wires are grown very close together, their growth rate will be relatively low, because the wires have to compete with each other to absorb the available vapor. On the other hand, when a wire is grown completely isolated, the wire will grow relatively fast, because it can absorb all the available vapor [14].

3.3 Annular milling with the focused ion beam (FIB)

Another commonly used method to prepare samples for atom probe analysis, involves the use of a focused ion beam (FIB). This device uses a focused beam of ions (usually gallium) for imaging purposes. But by increasing the current of the gallium ion source, the FIB can also be used to remove much more material from the sample than is needed for an image.

With those higher currents, it's possible to use the FIB for patterning or milling purposes, which makes the FIB a great tool to prepare specimens for atom probe analysis. The milling technique can be used to remove unwanted materials from a specimen, but also to make a sharp atom probe tip from a bulk material. In our case, for example, it's possible to isolate one single nanowire by milling away all material

in a circle around that specific wire and leaving only one standing in the middle of that circle. The results of this technique is shown in the images below.

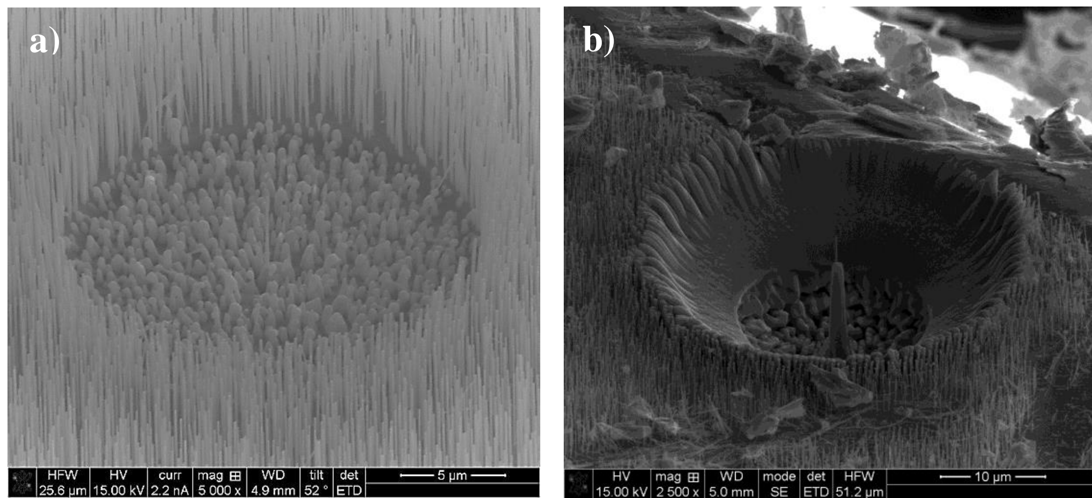

Figure 7: Annular FIB-milling applied to a sample of nanowires to isolate one single wire on a substrate. In the left picture (a) all nanowires are removed within a circle around one wire, in the right picture (b) the wires are removed as well as a part of the substrate.

The milling procedure, however, has a few drawbacks. The FIB, for example, deposits gallium from the ion source on the surface of the specimen, which will be detected during the atom probe measurement. It's also possible that the gallium ions or any removed materials damage the specimen during the sample preparation. A third problem, which might occur (especially in the case of figure 7b) is that the topography of the edges of the milled circle could modify the electric field around the isolated nanowire, resulting in a punch-through from the electrode to the substrate. The creation of edges should therefore be avoided as much as possible.

3.4 In situ lift-out of nanowires with a micromanipulator

By equipping a FIB with a micromanipulator, it's possible to lift-out a single wire from the substrate. A micromanipulator is a small controllable arm, which provides the ability to interact with a sample after it's loaded into the vacuum chamber of, for instance, a FIB. It can be used to move things around on a sample very precisely.

In our case, the tool can be used to pick a nanowire up from the substrate and mount it on top of a premade microtip. After the wire is firmly attached (the wire is welded to the microtip with for example platinum), the entire microtip can be loaded into the atom probe for atom probe analysis. The process of picking a nanowire up (a) and attaching it to a microtip (b) is illustrated in figure 8.

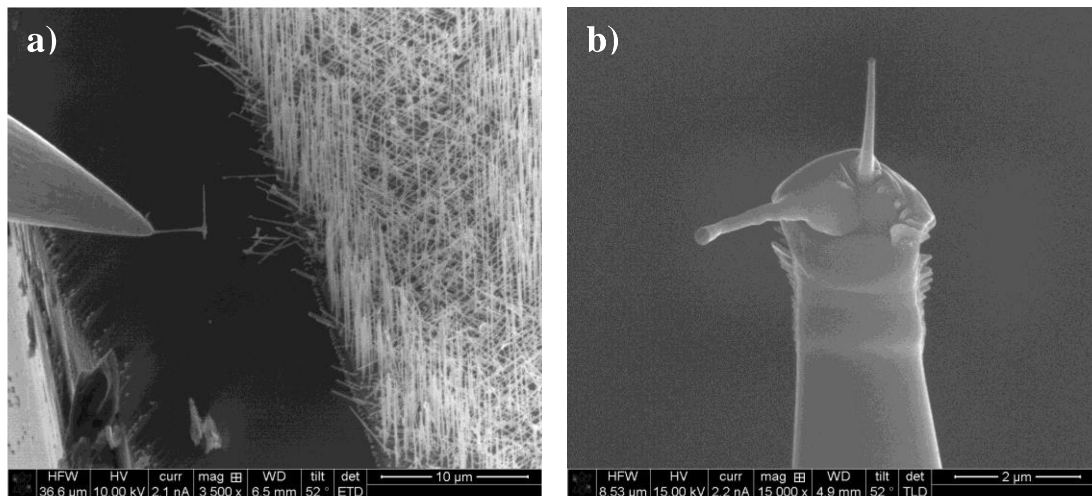

Figure 8: In-situ lift-out of nanowires with a micromanipulator. The left figure (a) shows how a nanowire is picked up and the right figure (b) shows how the nanowire is attached to the microtip.

This isolation method has a few advantages compared to the annular milling method. Since the micromanipulator can be controlled very precisely, there is less risk of ruining the specimen during the preparation and since the ion source of the FIB isn't used at all, the specimen will contain no extra gallium from the FIB. However, this method takes a lot of time and its success mainly depends on whether the attachment of the nanowire to the microtip is strong enough to endure the applied electric field.

3.5 'Crushing' nanowires with a mask

All three procedures that are discussed above, can be used to isolate a single nanowire. During this project, it's investigated whether it is possible to isolate a wire by pressing a mask (a silicon piece with holes in it) against a sample of nanowires. Hopefully, all nanowires will be pressed down or break off, except for the single wire that goes through the hole within the mask.

To do this, the mask is attached to one side of an optical table by carbon tape, while the sample with nanowires is attached to the opposite side of the same table (see figure 9 below). It's very important that the mask and the sample are well aligned, otherwise they won't hit each other. By turning the screw of the optical table, the mask will be pressed against the sample, crushing the nanowires during the process. The holes in the mask will hopefully result in patches of uncrushed nanowires, surrounded by broken or bended wires.

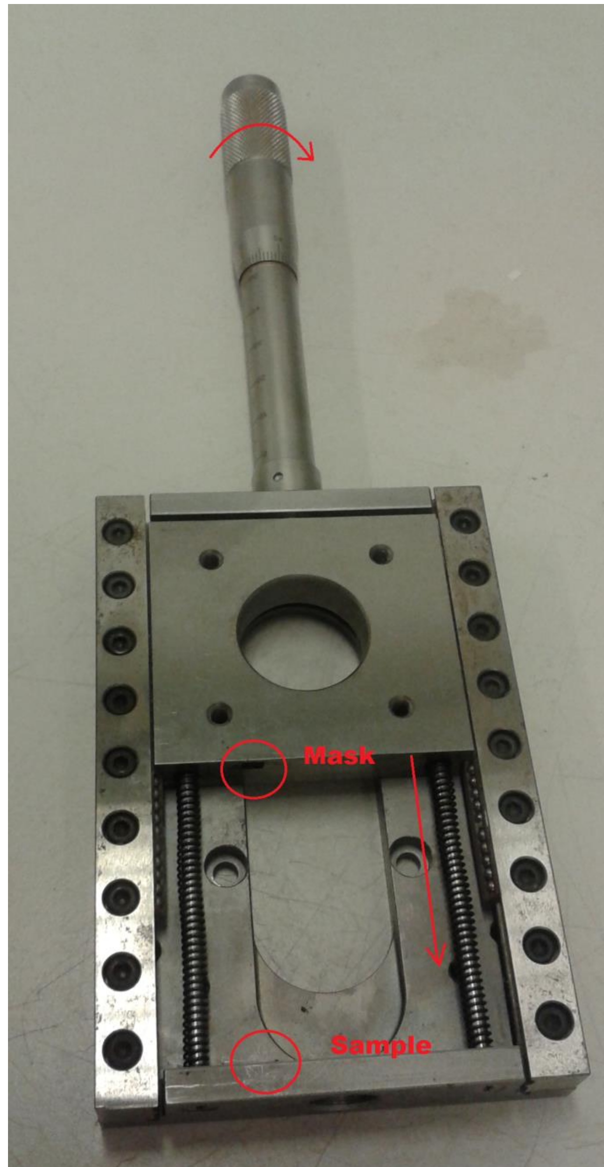

Figure 9: This picture shows the setup and explains how it's used to 'crush' a sample of nanowires.

The results of this isolation method and the problems that are encountered, are discussed in the next chapter.

4 Results

4.1 Crushing nanowires with a mask

As mentioned in the previous chapter, the possibility of ‘crushing’ a sample of nanowires with a mask to prepare it for atom probe analysis, is investigated. The used mask is made out of a flat piece of silicon, in which holes are made using the focused ion beam (FIB). During the project, a few different masks with different patterns have been used. Two examples are shown in figure 10 below.

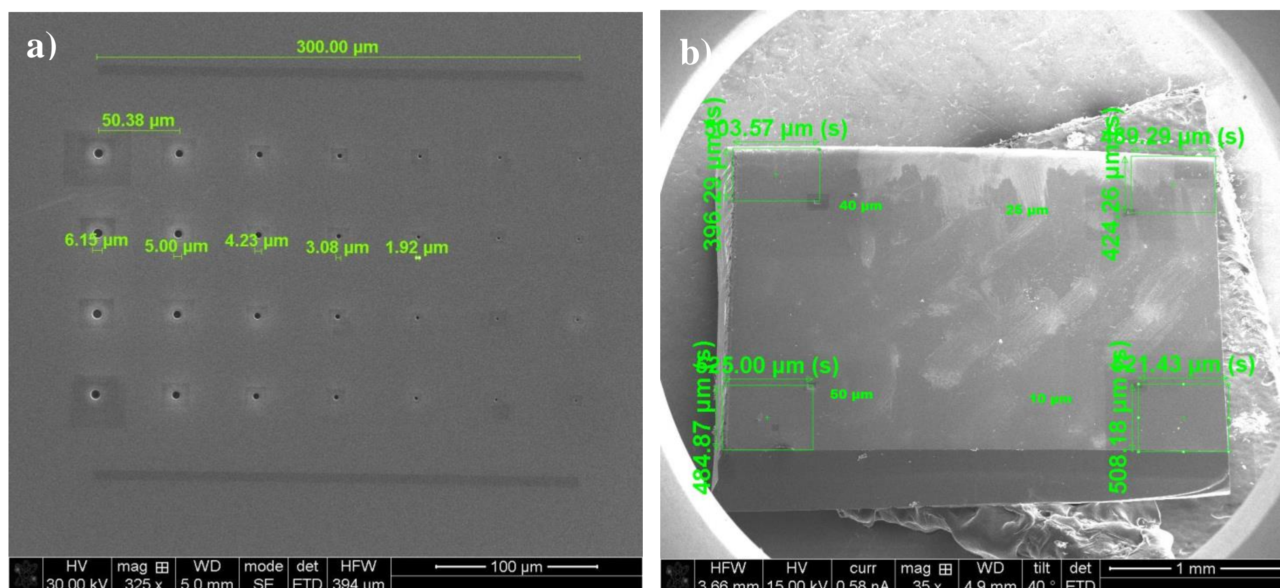

Figure 10: These are images showing the designs of two different masks that were used. The left picture (a) shows the first mask that has been made (mask 1), the right picture (b) shows the second mask (mask 2). The holes in mask 1 are rather small and round, while the holes in mask 2 are square-shaped and much bigger. The holes in the different rows in mask 1 are identical to each other.

The experiments were started with mask 1. However, because of the small size of the holes, the pattern of the mask couldn’t be found on the crushed sample. In other words, it wasn’t possible to see whether there were patches of wires left standing, next to the broken wires. Consequently, it wasn’t possible to determine whether the method was successful or not.

Therefore, a new mask (mask 2) was created with much larger holes, ranging between 50 μm^2 and 10 μm^2, as can be seen in figure 10b above. All of these holes resulted in clearly visible patches of standing nanowires, as can be seen in figure 11 below:

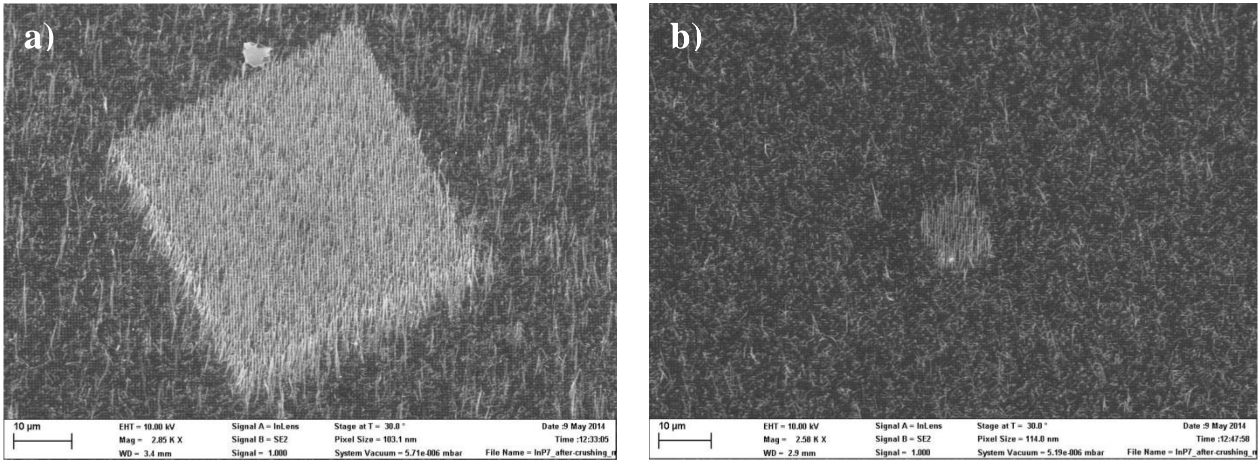

Figure 11:These are images of the patches of nanowires created by mask 2 on sample 1 (see table 1 in appendix A for more information). The left picture (a) shows the 50 μm^2 patch and the right picture (b) shows the 10 μm^2 patch. The 40 μm^2 and the 25 μm^2 patches, that are also on the mask, could also be found on the sample.

Figure 11 shows that the 'crushing'-method can be used successfully to remove a lot of standing nanowires from the substrate. However, there are still way too many nanowires in the created patches to use them for atom probe analysis and the substrate isn't yet clean enough, since the crushed nanowires are still lying on the substrate.

4.2 In search for the smallest possible hole

To solve this problem, smaller holes (similar to the ones in mask 1) were created next to the big holes in mask 2. The new design of mask 2 is shown in figure 12.

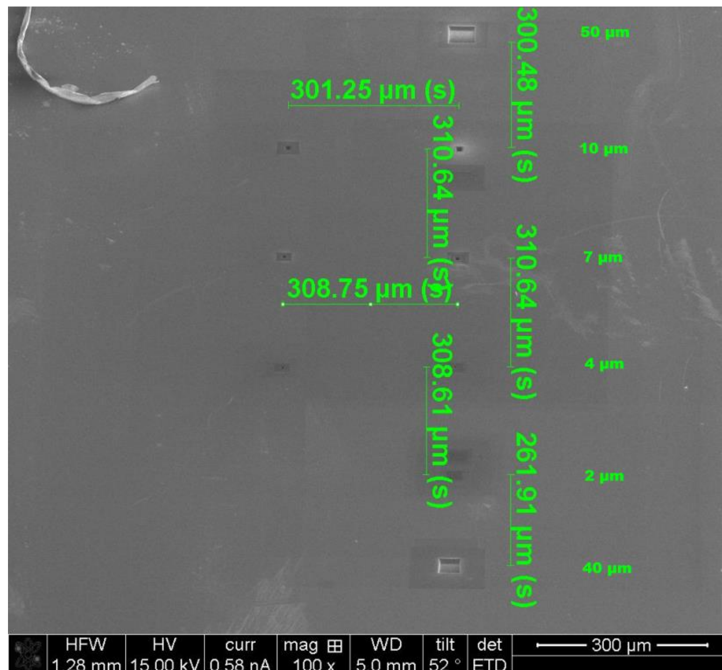

Figure 12:This is a FIB-image which shows the design of mask 2 after extending it with smaller holes. The holes in the right column are square-shaped, while the holes in the left column are circles.

When analyzing a sample crushed by this new mask with a scanning electron microscope (SEM), the big patches of 50 µm^2 and 40 µm^2 can easily be found upon the substrate, just like in the previous experiments (see figure 11). However, because the positions of the smaller holes are known compared to the big ones, it was this time also possible to find the smaller patches of standing nanowires created by the smaller holes in the mask. These patches are shown in figure 13 below. This is in contrast with the failed experiments with mask 1 in which the patches had roughly the same size, but could not be found.

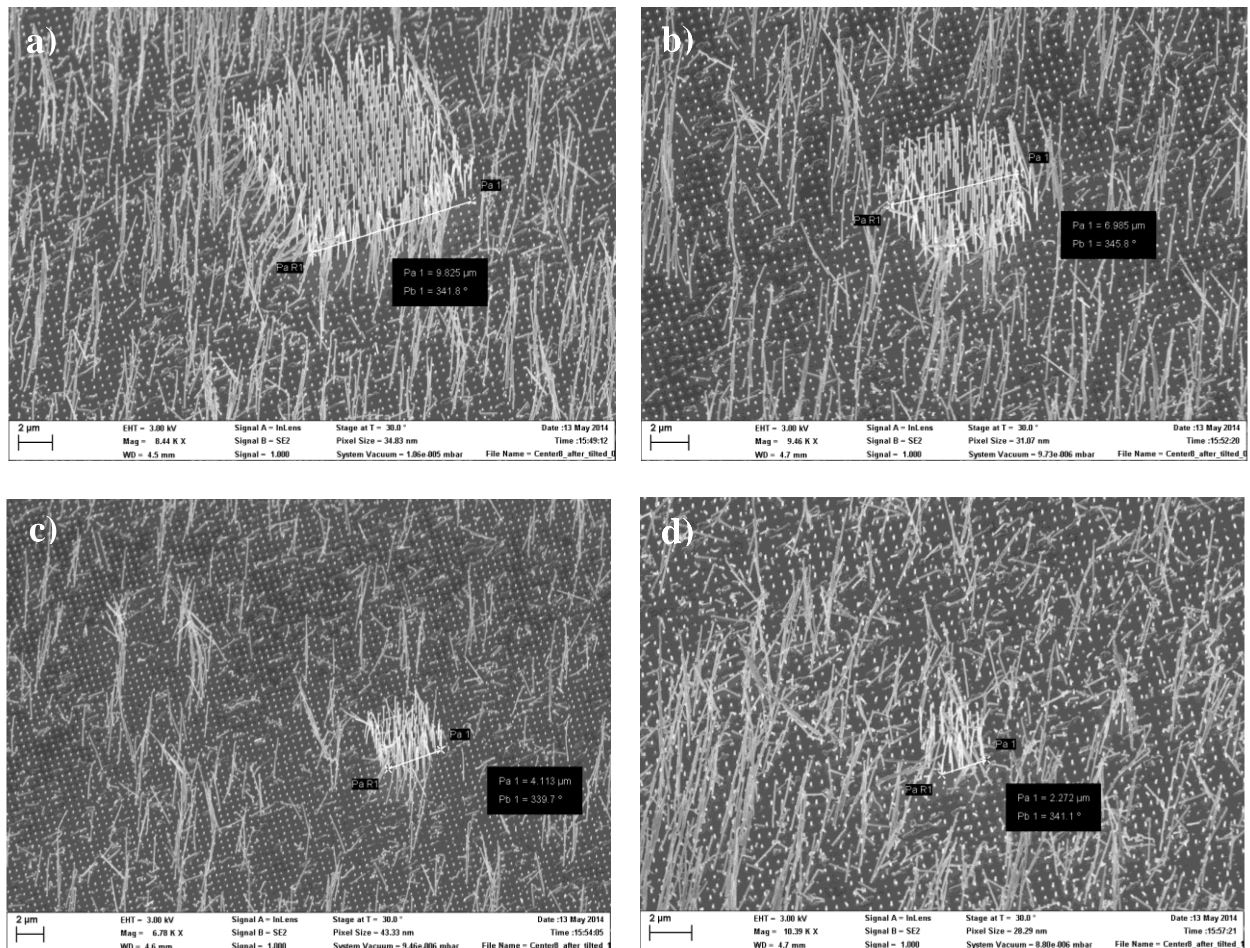

Figure 13:These are SEM-images of the small patches of standing nanowires on sample 1 created by the modified mask 2. Picture (a) shows the square-shaped 10 µm^2 patch, picture (b) shows the 7 µm^2 patch, picture (c) the 4 µm^2 patch and picture (d) the 2 µm^2 patch.

This experiment has been repeated several times to verify that all of these patches can be found on the sample after each attempt. This wasn't the case for the 2 µm^2, which was only recognizable once (see figure 13d). This isn't entirely unexpected, because the smallest patch gets destroyed the easiest. A small movement of the mask during the experiment could result in a destroyed patch, but also other nanowires (which have been broken or bended by the mask) could damage the patch during the crushing process.

According to the results of this experiment, it seems to be impossible to isolate one single wire using only this crushing procedure. The smallest viable hole in the mask

for this kind of sample seems to be the 4 μm^2 one, while it can only be found, when its position is roughly known beforehand.

4.3 Complete isolation of a single wire

Since there are, roughly estimated, still 100 nanowires left standing in the smallest patch (the 4 μm^2 patch), the 'crushing'-procedure isn't sufficient enough to prepare samples for APT. Therefore, another technique should be used to complete the isolation and keep only one wire left standing. Annular FIB-milling, which is described in paragraph 3.3, is perfect to further reduce the amount of standing nanowires on the substrate, as can be seen in figure 14a below.

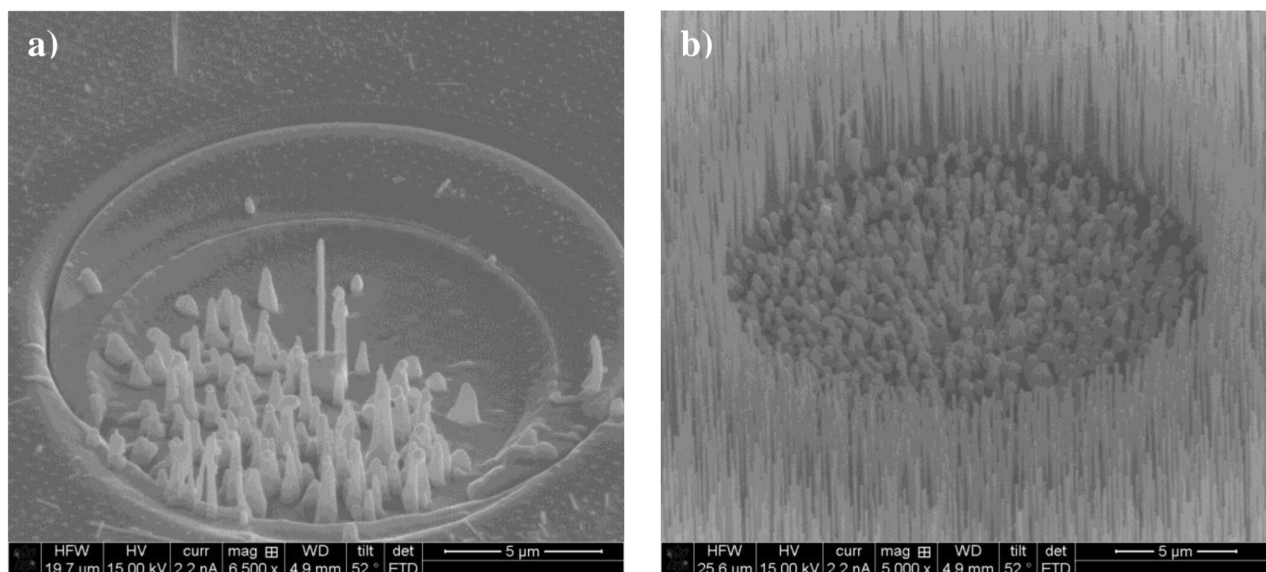

Figure 14: These pictures illustrate how FIB-milling can be used to finish the isolation of one single nanowire. The sample in the left image (a) is crushed with mask 2 before the remainder of the patch is milled away by the FIB. The right image (b) shows how the isolated wire would look like when the sample wasn't crushed beforehand. Both of these samples were of type 2 (see appendix A).

The big advantage of crushing the sample before FIB-milling is that the substrate is relatively empty and there are almost no wires left standing at the edge of the milled circle, which is the case with an uncrushed sample (see figure 14b).

Since FIB-milling is necessary to isolate a wire, it's not necessary to make extremely small patches, because larger patches are easier to find in the FIB. However, the patches shouldn't be too big either to minimalize the area that has to be milled. That's why the new mask (mask 2 broke into two pieces during an experiment and a new mask had to be created) mainly contained holes from 25 μm^2 and 10 μm^2. Two bigger holes (50 m^2 and 40 μm^2) were added for navigation purposes, because they are easier to find. A picture of mask 3 is shown below:

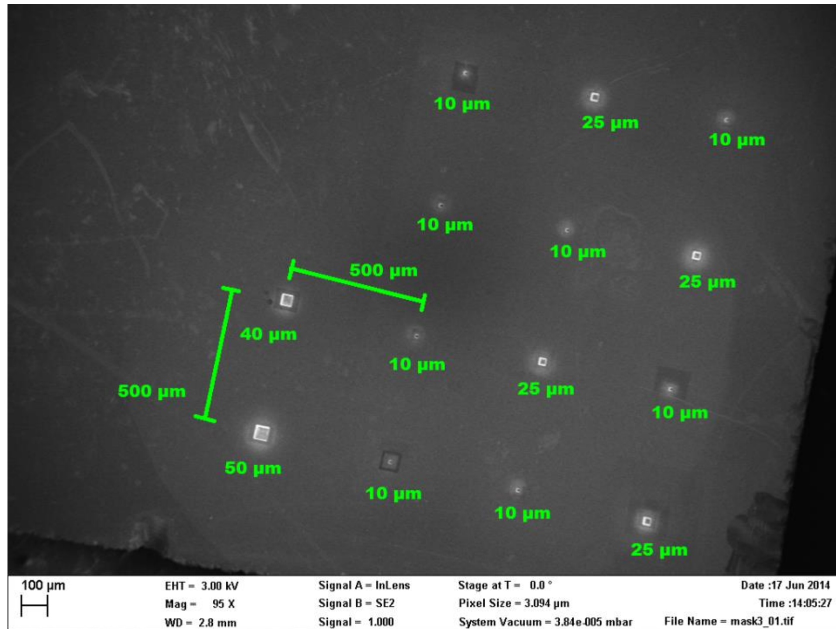

Figure 15: This is a SEM-image showing the design of mask 3.

4.4 Longer wires

The isolated nanowires shown in figure 14a above, looks like it could result in a good atom probe analysis. However, during the actual APT-measurement, it was discovered that the wires were too short, as a result of which the substrate was brought way too close to the local electrode. The presence of a flat substrate underneath the specimen, positioned too close to the top of the tip, causes a dramatic drop in the electric field [15], as a result of which the voltage applied to the wire became way too high.

Consequently, it was necessary to start experimenting with samples containing longer wires. The same procedure was used (crushing the sample with a mask, before completing the isolation by FIB-milling) to isolate wires on these samples. In the remainder of this paragraph, the encountered problems and the achieved results for these different samples are discussed.

4.4.1 Colloidal grown indium phosphide/indium arsenide nanowires

These nanowires (sample 3) exist of a combination of InP and InAs and are grown from colloids (see paragraph 2.2). This growth-method resulted in a more sparse and irregular array of nanowires compared to the previous samples grown by lithographic techniques (EBL and nanoimprint). Figure 16a shows one of these samples before it's crushed.

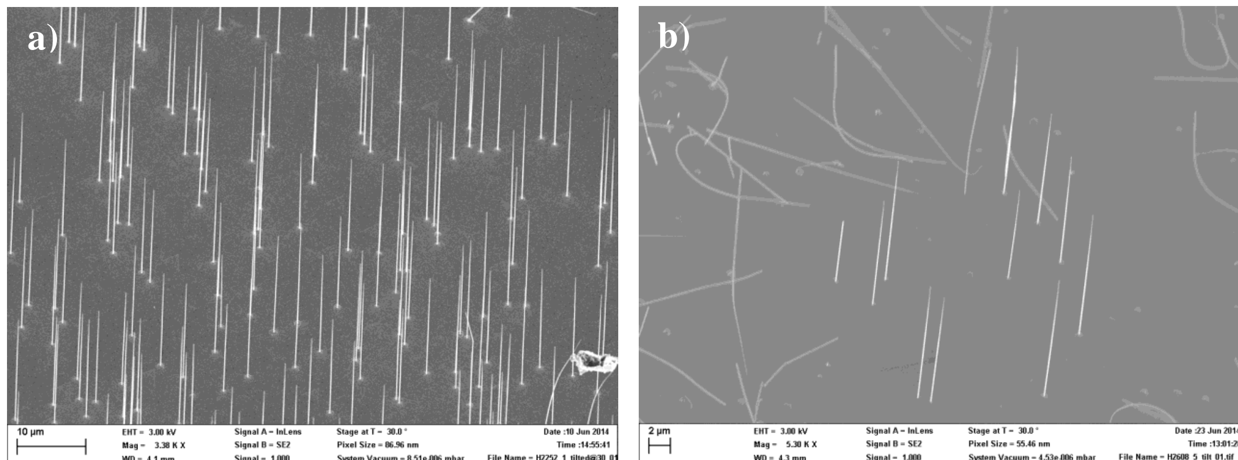

Figure 16: These are SEM-images of the colloid sample (sample 3) before crushing (a) and after crushing (b). On the right picture one of the patches created by mask 3 is shown.

The sample shown in figure 16a is crushed by mask 3, which resulted in figure 16b. Because of the irregularities and the large spacing between nanowires on this sample, a patch, created by the mask, can, for instance, contain only a few nanowires. This makes it difficult to find the patches created by the mask. However, when a patch has been found, it doesn't require a lot of FIB-milling anymore to isolate a single wire. For the sample shown above, two wires were prepared for APT and isolated from any other nanowires in their surroundings (see figure 17 below).

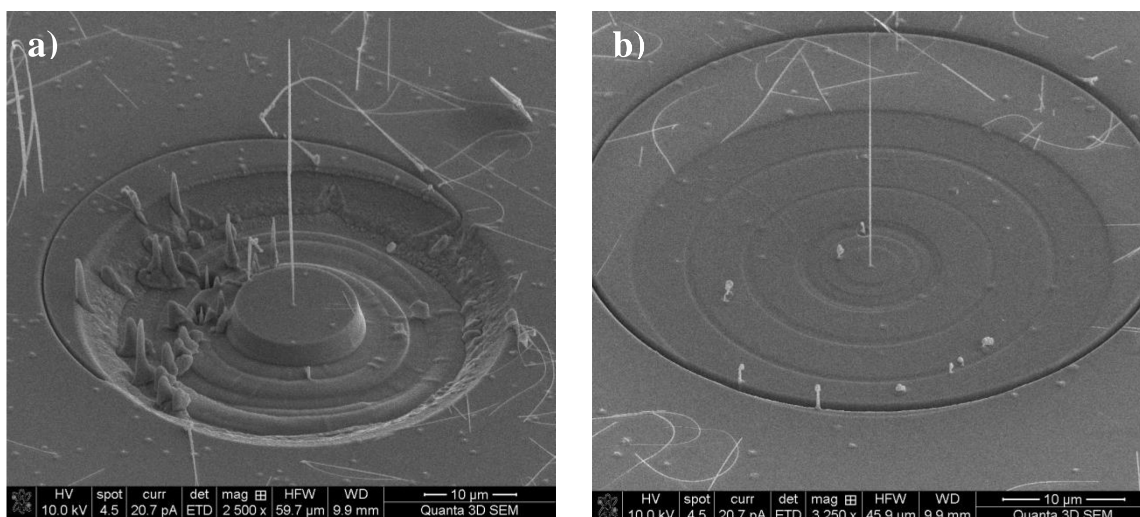

Figure 17: These images show two isolated wires on the substrate after crushing sample 3 with mask 3 and finishing the isolating by FIB-milling.

These nanowires shown in figure 17 above, were both used for APT. Unfortunately, both isolated wired didn't make it to the voltage at which atoms should start to evaporate, since the first wire was ripped out of the substrate and the second wire bended over, as can be seen in figure 18 below.

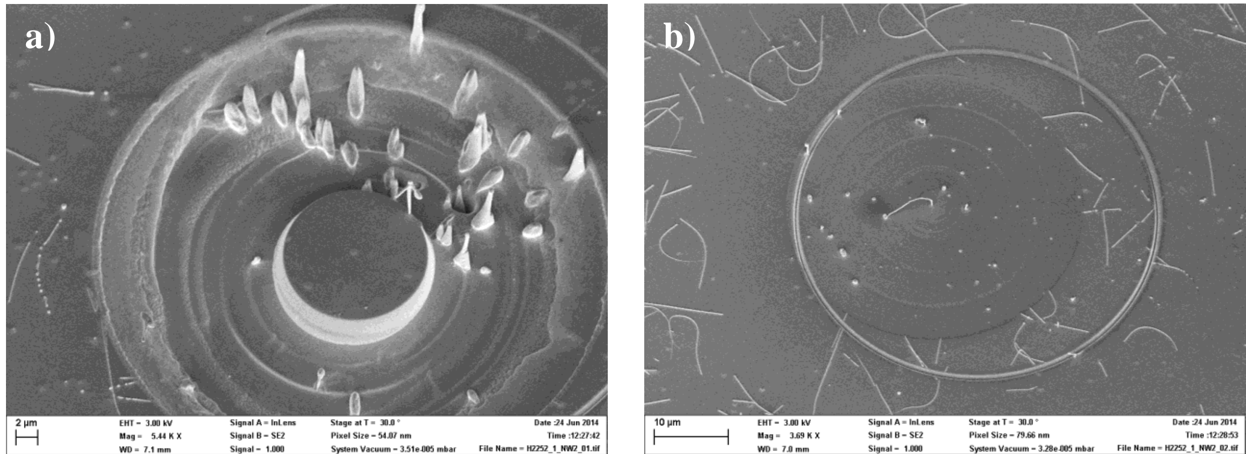

Figure 18: These SEM-images show what happened to the isolated wire on sample 3 after atom probe analysis. The wire on the left picture (a) was ripped out of the substrate roughly at 800V and the wire on the right picture (b) bended over at around 750V for some reason.

Concluding from the atom probe measurement of the first wire (which was ripped out at only 800V), the nanowires on these samples aren't firmly enough attached to the substrate. It's therefore useless to continue using this isolation method on these nanowires. The pick-up method, described in paragraph 3.4, could be an alternative method to prepare these wires for APT, since they need to be firmly welded to the microtips.

4.4.2 Dense germanium nanowires on a germanium substrate

So, we moved on to the next kind of sample (sample 4), contained long germanium wires grown on a germanium substrate with a rather small interspacing between the wires. Because the sample had previously been flipped over, it contained an area of bended wires, as can be seen in the SEM-image taken before crushing the sample (figure 19a). This, however, does not influence the results of the crushing-experiment, because the mask is targeted at an area containing only straight wires.

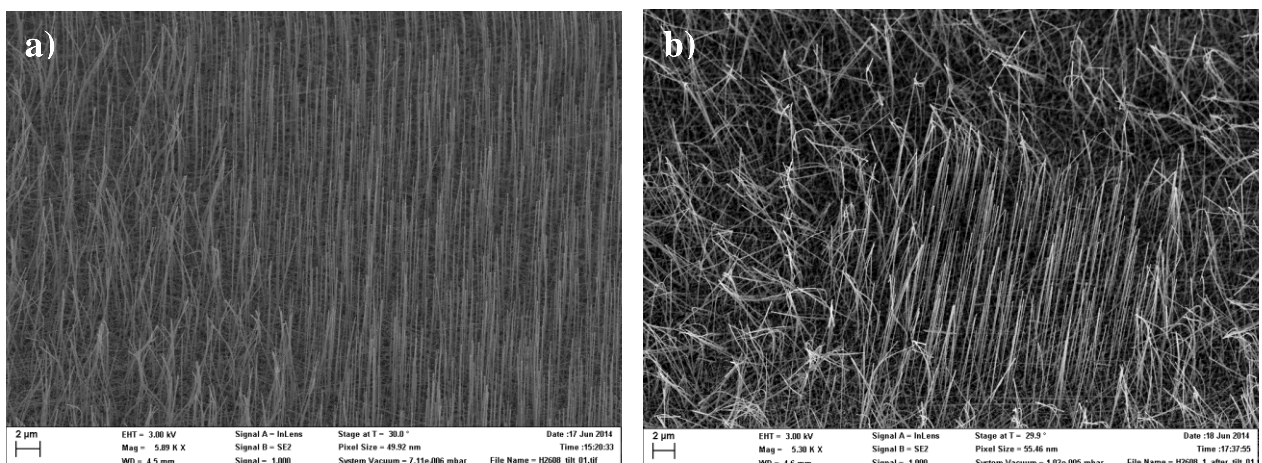

Figure 19: These are SEM-images of the germanium sample (sample 4) before crushing (a) and after crushing (b). Some nanowires were already bended before crushing the sample, which is confirmed by the left picture. The right picture shows a patch created by mask 3.

After crushing the sample with mask 3, the created patches of wires could be found pretty easily (figure 19b). However, they are less isolated than intended, because most of the nanowires aren't removed from the substrate. The wires appear to bend rather than break. It's nevertheless possible to prepare an isolated wire by FIB-milling (see figure 20 below), but only if the chosen wire is free-standing and not in contact with any of the other (standing or bended) wires that need to be removed.

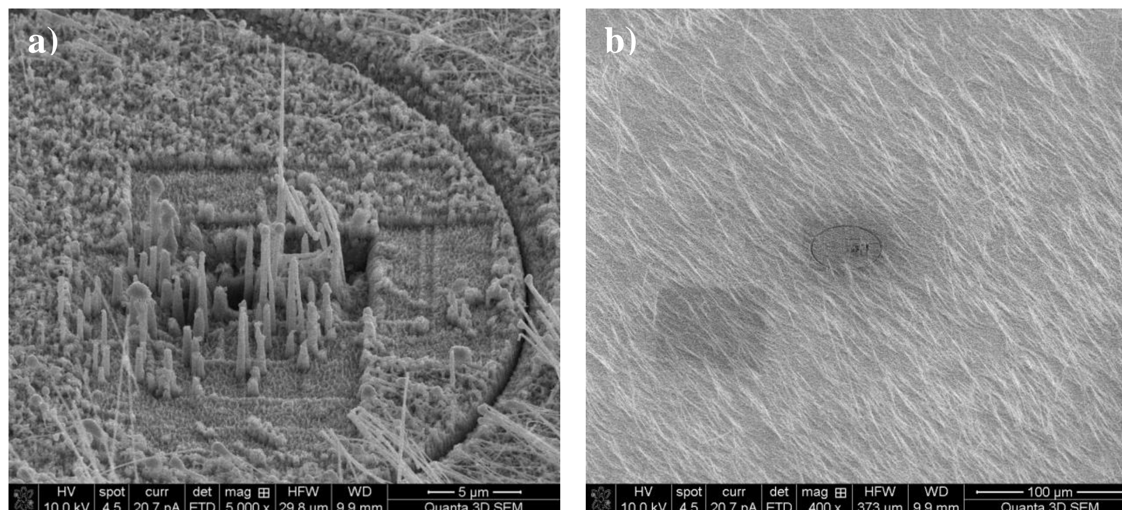

Figure 20: These pictures show an isolated wire on the germanium sample (sample 4) after crushing and FIB-milling. The left picture (a) shows a close-up of the isolated wire, the right picture (b) shows the surroundings of this wire.

The nanowire (shown in figure 20a) itself is nicely isolated and would be perfect for APT, but the substrate around the isolated wire is still far from clean, as can been seen in figure 20b. This is, of course, again caused by the fact that these wires apparently rather bend than break (which was previously already discovered). In principle those lying nanowires shouldn't be a problem for the APT-measurement, since they are not directly near the isolated wire. However, it wasn't possible to target the laser (for laser pulsing mode) onto the isolated wire to start the measurement, because the lying wires blocked the view of the microscopes of the atom probe and the isolated wire could therefore not be found. In addition, the crushed nanowires may get sucked onto the electrode when the voltage is applied.

4.5 Improving the crushing method

The failed experiment with the germanium nanowires increased the need for an improved crushing method, which removes wires instead of just pressing them down on the substrate. Most of the broken wires should rather stick to the mask than to the substrate. There are a lot of different ways to achieve this and the best way has yet to be determined. In the remainder of this paragraph, a few small test will be discussed, that were aimed at improving the crushing method. However, more research should be done, before the discussed improvements are implemented.

4.5.1 Depositing a sticky layer on top of the mask

One possible way to make sure that the wires stick to the mask instead of the substrate after crushing, is by depositing an extra sticky layer on top of the mask. A few different sticky layers were tried (for example, gel and tape) and the best results were achieved with a layer of PDMS. PDMS is a silicon-based organic polymer, which is soft (almost liquid) after its preparation, but after some time (or after heating) it gets cured, increasing its viscosity enormously.

In figure 21 below, the results of crushing a sample of indium phosphide nanowires with a PDMS covered mask are shown. However, as the sticky properties of the PDMS layer vary over time, the crushing-experiment is repeated after several curing times.

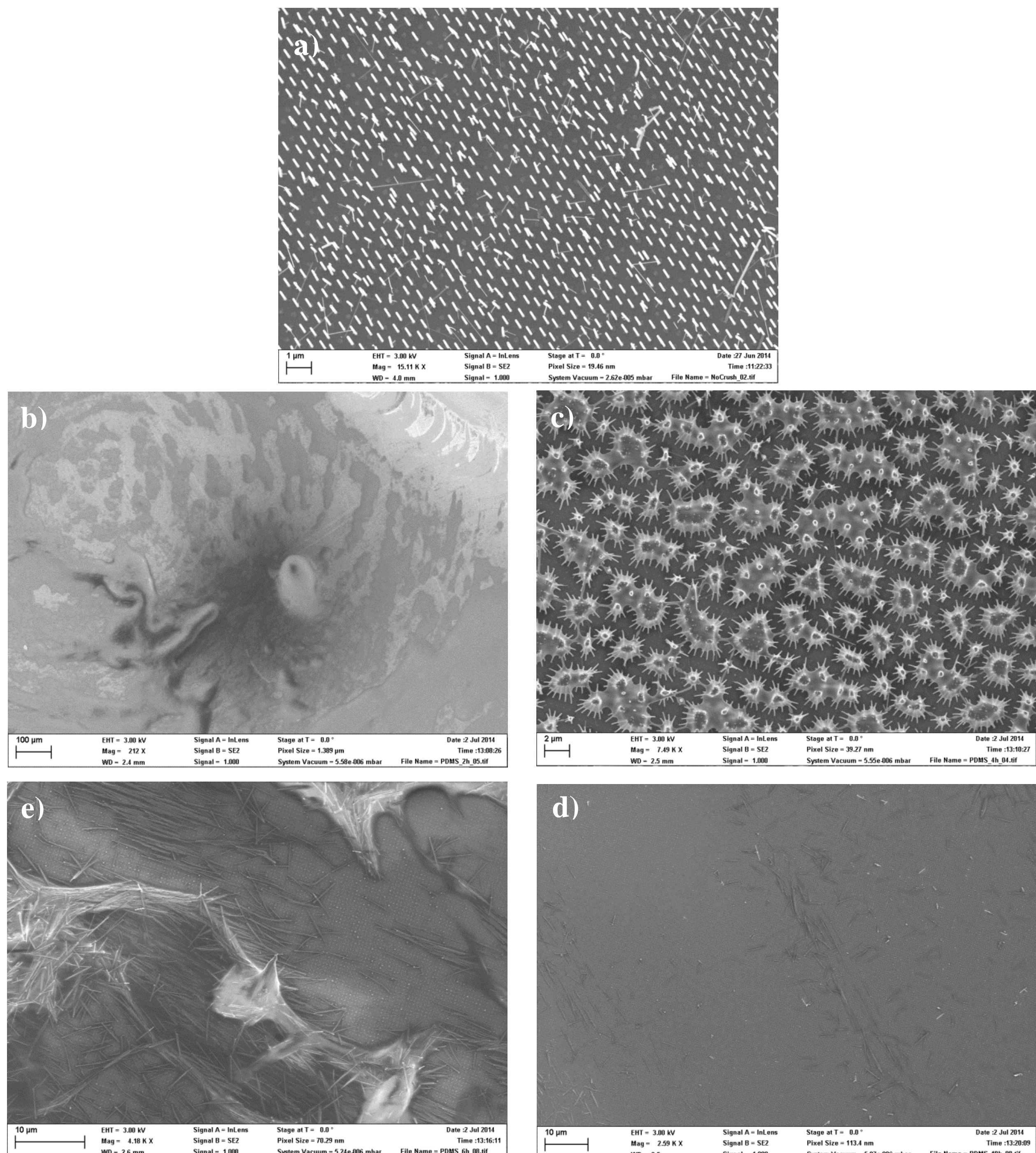

Figure 21: These pictures show the results of the crushing method when the mask is covered with a small layer of PDMS. Picture (a) shows the sample (type 2 in appendix A), which was used for this test. Picture (b) till (e) show the same sample (different locations) after it's crushed with a PDMS-mask after respectively 2 hours (b), 4 hours (c), 6 hours (d) and 19 hours (e) of curing time.

The pictures from figure 21 show some varying results. After two hours (figure 21b) the PDMS is clearly still too liquid, because a large part of the liquid PDMS was transferred to the sample during the crushing process. After 4 hours of curing time (figure 21c), the wires are pushed inside the PDMS. After releasing the mask, a little bit of PDMS keeps covering the nanowires, causing them to cluster together. After 6 hours (figure 21d), the method starts working, however, most of the wires are still pressed down and covered with a small layer of PDMS afterwards. And after 19 hours of curing time (figure 21e) the crushing method seems to work best, in large areas most of the wires were completely removed from the substrate.

When using a sticky layer on top of the mask, it doesn't matter which layer, it's important the holes are kept open. In the previously discussed experiment, a flat piece of silicon (without any holes) was used to crush the sample. So, whether the PDMS layer also works for the mask, should still be confirmed.

4.5.2 Ripping the wires from the substrate

Another possible way to remove most of the wires from the substrate, is by tearing them away from the substrate. This can be done by (partially) sticking the wires inside a layer of PDMS. As soon as that's the case, the PDMS is cured completely by waiting or by heating it up. After the PDMS is cured and the wires are still firmly captured within the layer, the PDMS-mask is pulled up, ripping the wires from the substrate during the process.

While doing this, it's again important that the layer of PDMS doesn't cover the holes. By looking sideways with an optical microscope, it's possible to determine whether the tops of the nanowires are already sticking inside the PDMS or not.

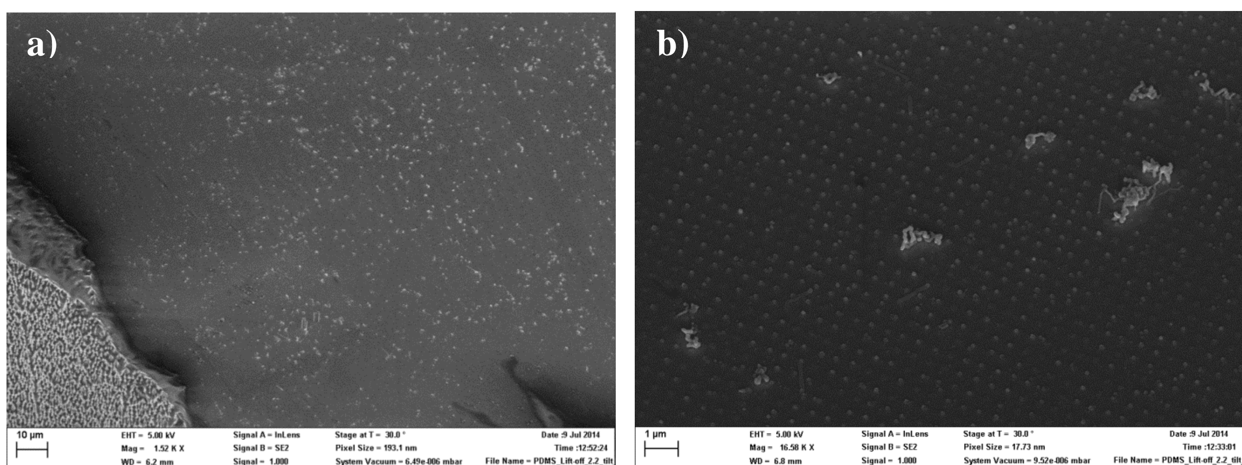

Figure 22: These picture show the results of the 'rip out'-method, which was again applied to a sample of type 2. The right picture (b) is a close-up of the white dots in the left picture (a).

The results shown in figure 22 confirm that this method works fine: almost all standing nanowires are completely removed from the substrate. The only ‘things’ that are still present at the substrate (see figure 22b) are randomly grown from the gold droplets during the VLS-growth of the nanowires. Consequently, these things are also made from indium phosphide. However, it doesn’t matter for the APT-measurement that these things aren’t removed, mainly because they are very small and probably firmly attached to the substrate (even better than the nanowires, since they cover a bigger area).

While scanning over the surface of the substrate, a patch containing a few nanowires was also encountered (see figure 23 below). The fact that these wires are still standing was, strangely enough, not caused by one of the holes within the mask, because the position of this patch didn’t match with the position of the holes. After analyzing the mask, however, it was discovered that there was a small gap in the PDMS layer, probably caused by some kind of air bubble, which has enabled these wires to keep standing.

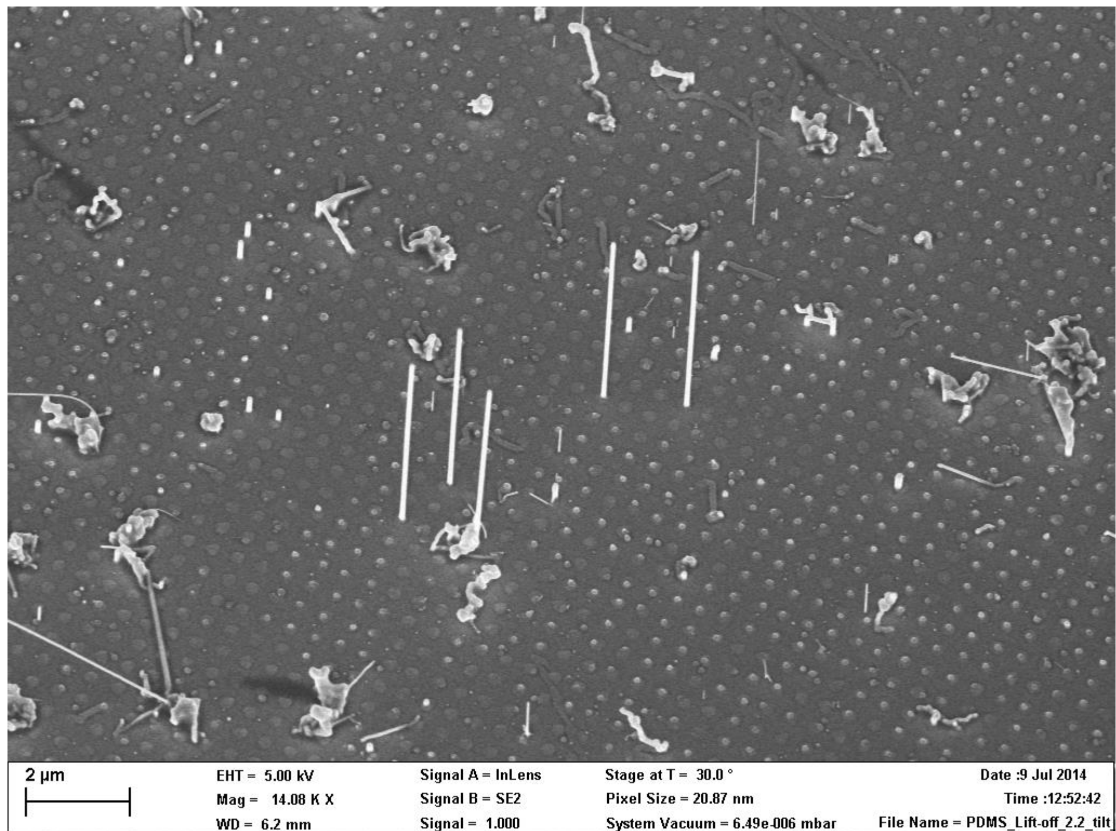

Figure 23: There are even a few nanowires left standing after the 'rip out'-method.

5 Discussion and conclusion

The initial goal of this project was to develop a method to prepare a sample with nanowires for atom probe tomography (APT), in such a way that the measurement could be done directly on the substrate. To achieve this, it should be made sure that all atoms are evaporated from the same nanowire. Therefore, this wire should be isolated from all other standing wires within a radius of a few hundred micrometer.

During the first step of the proposed isolation process, a mask is pressed upon the substrate, while breaking or pressing down the standing nanowires. In principle, it would be possible that only one wire goes through one of the holes within the mask and keeps standing, but this can only happen when the holes are small enough. Unfortunately this cannot be the case, since the size of the smallest viable hole appears to be 4 μm^2. It's therefore impossible to isolate one single nanowire by 'crushing' the sample. However, it's still worth doing so, because it does remove a lot of unwanted wires from the substrate.

The 4 μm^2 patch, created by the smallest hole, still roughly contains 100 nanowires, which are way too many for APT. That's why a second step is added to the isolation procedure. After the sample is crushed, all standing wires in a patch, created by the mask, are milled away by the focused ion beam (FIB), except one.

The combination of crushing and milling results in perfectly isolated wires, as shown in figure 14, figure 17 and figure 20. These wires are well prepared and ready for atom probe analysis. Nevertheless, none of these isolated nanowires have resulted in a good APT-measurement, because of the following problems that were encountered:

- Sample 1 and 2: The indium phosphide nanowires (as shown in figure 14) were very small. To evaporate atoms from these wires, the electrode had to be moved very close to the substrate, as a result of which the voltage applied to the wire becomes too high.
- Sample 3: The indium phosphide/indium arsenide nanowires (as shown in figure 17) were not good enough attached to the substrate, causing them to get ripped out of the substrate by the electric field (see figure 18a).
- Sample 4: The germanium wires rather bend than break during the crushing process. Consequently, the substrate around the isolated wire is far from clean (see figure 20), making it impossible to find the isolated wires with the microscopes of the atom probe, which is necessary to target the laser.

The first two of these problems are depending on the type of used nanowires and are not influenced by this isolation procedure. The third problem, however, is something which could (and should) be solved by improving the crushing step within the process. This can be done by making sure that the nanowires rather stick to the mask than to the substrate (see paragraph 4.5).

Nevertheless, the proposed isolation method has provided some well-isolated wires. However, the method can still be improved to achieve better results, which might even be necessary, because the results of the crushing-step vary quite a lot depending on which type of sample is used. Whether the actual atom probe measurement will work, after the isolation of a wire, does generally not depend on the isolation procedure, but on the type of sample which is used.

6 Literature

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Appendix A: List of used nanowire samples

All nanowire samples that were used during this project are grown in the Hermes-reactor at the campus of the Technical University Eindhoven. The table below lists the different samples that were used during these experiments. The table also includes information about the growth of the nanowires, their chemical composition and their dimension.

Table 1:A table showing the different kinds of samples that were used during the experiments.

Sample-number	H-number	Material	Substrate	Growth-method	Length (approx.)	Spacing (approx.)
1	H2265	InP	InP [100]	Nanoimprint	3.5 µm	500 nm
2	H1336	InP	InP [111]	Nanoimprint	4.5 µm	500 nm
3	H2252	InP/InAs	InP [111]	Colloids	30 µm	very irregular
4	H2608	Ge	Ge [111]	Not known	15 µm	irregular ≈ 1 µm