

Christoph Amtmann

Applications of Multi-Walled Carbon Nano Tubes in a Scanning Electron Microscope

Bachelor Thesis

For obtaining the academic degree
Bachelor of Science

Bachelor Program of Technical Physics



Graz University of Technology

Supervisor:
Univ.-Prof. Ph.D. Peter Hadley
Institute of Solid State Physics

Graz, April 25, 2012

Acknowledgement

I want to acknowledge my supervisor Univ.-Prof. Ph.D. Peter Hadley for supporting me at my bachelor thesis. I want to thank him, for giving me the possibility to write about a topic I chose, to work independently and to follow my own ideas. I also want to thank Stefan Kirnstötter and Martin Mario Faccinelli for guiding me in the laboratory and supporting my experiments.

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1 Motivation

The Institute of Solid State Physics of the TU Graz uses a scanning electron microscope for investigation of semiconductor properties. Therefore some manipulators are mounted in the microscope to make contact to the surface of the samples in order to measure electrical and mechanical properties. Tungsten tips are used generally with a top diameter in the range of 1 μm . Tungsten is a strong material, but the tips bend after several times of using. This causes problems because the exact point of contact in the scanning electron microscope is not longer visible and so exact measurements can not be made.

The aim of this bachelor thesis is to stick a multi-walled carbon nano tube on the top of the tip, in order to produce a flexible and good conducting junction.

2 State of the Art

Before this thesis some experiments were made with multi-walled carbon nano tubes (MWCNTs). The electric resistance of a PET covered with single-walled carbon nano tubes (SWCNTs) was measured and some experiments with clumps of MWCNTs were made. The tip, which was mounted in the scanning electron microscope, was put into a clump and some tubes stuck to the metal surface.

Also the production of sharp platinum-iridium tips was known. The bachelor student Martin Kupper wrote his thesis about producing tips by electrochemical etching, *Very Sharp Platinum-Iridium Tips* [1]. He found a simple way to get tips with a top diameter less than 100 nm. In his thesis he describes all working steps and the used etching programs.

3 Carbon Nano Tubes

Since their discovery in 1991, carbon nano tubes (CNTs) have become a big hope for the future in nano technologies. Not only in the semiconductor industry, also in the biomedical and chemical industry. The range of applications is enormous.

3.1 Structure and Size

A carbon nano tube consists of single carbon atoms. The atoms are arranged on a hexagonal lattice and this is rolled like a cylinder. A single layer of carbon is called graphene. Depending on the rolling way of the cylinder there are 3 different structures. Figure 1 shows the structure of the lattice and the different ways to roll them. The indices (n,m) in combination with the lattice vectors a_1 and a_2 represent the rolling directions. If $m = n$ the tube is called armchair, if $m = 0$ the tube is called zigzag and the a rolling directions in-between those are called ciral. [2]

CNTs with one layer of carbon are called single-walled nano tubes (SWCNT). CNTs with more than one layer of carbon are called Multi-walled carbon nano tubes (MWCNT). The single layers of graphene are connected by Van-der -Waals forces. These forces are also responsible for CNTs sticking to each other or to other materials.

The tubes exist in a various range of sizes. The diameters of SWCNTs are in range of 1 nm with a length up to several micrometers . The MWCNTs are much bigger, diameters at the size of tens of nano meters and lengths in the range of tens of micrometers.

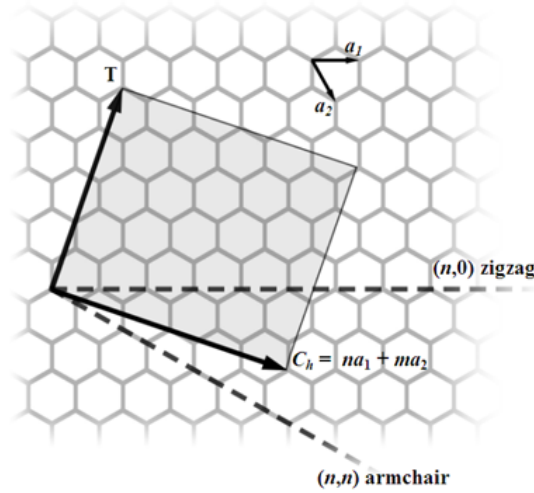


Figure 1: Hexagonal lattice of a single carbon layer. T is the tube axis and $c_h = na_1 + ma_2$ shows how the CNT is rolled. [3]

3.2 Electrical, Thermal and Mechanical Properties

The electrical properties depend on the rolling directions. If $n - m$ is multiple of 3, they have a metallic behaviour. Otherwise it is semiconducting [2]. The band structure is visible in figure 2. For a very detailed paper about electrical properties see [4]. Carbon nano tubes are good thermal conductors in the direction of their axis and they are insulators orthonormal to their axis. The conductivity is better than diamond and so the best, which is known so far. A table of a comparison of CNTs with other material is listed in this paper *Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review* [9]. Mechanically, CNTs are much stronger than steel but lighter. The density of CNTs is a sixth of steel. A comparison between CNTs and other materials is found in table 1.

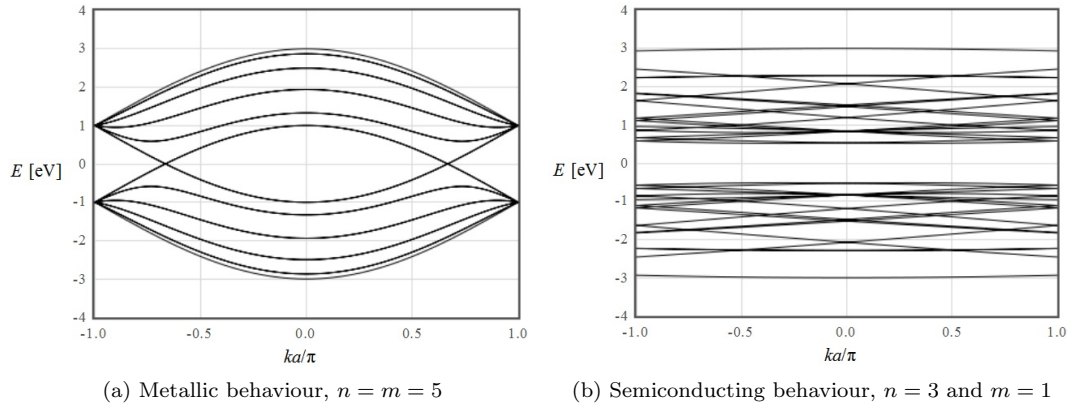


Figure 2: Tight binding dispersion relation of SWCNTs. [5]

Table 1: Young's modulus, tensile strength and density of CNTs compared with other materials.[7]

| Material | Young's modulus / GPa | Tensile Strength / GPa | Density / $\text{g}\cdot\text{cm}^{-3}$ |
|----------|-----------------------|------------------------|---|
| SWCNT | 1054.000 | 150.000 | |
| MWCNT | 1200.000 | 150.000 | 2.600 |
| Steel | 208.000 | 0.400 | 7.800 |
| Epoxy | 3.500 | 0.005 | 1.250 |
| Wood | 16.000 | 0.008 | 0.600 |

3.3 Production of Carbon Nano Tubes

Carbon nano tubes can be found in low concentrations in the nature, for example in a normal flame. But for industrial production high developed devices are needed to get pure and homogeneous nano tubes. There are several methods to produce them, like carbon

arc-discharge, laser ablation, high pressure carbon monoxide (HiPco) and chemical vapor deposition (CVD) [8].

3.4 Description of Papers used in this Thesis

Some of the processes, used in this thesis, were found in papers. In the following section there is a description of the papers and the differences between the written method and the realised one are pointed out.

The method of suspending the tubes with sodium dodecyl sulfate (SDS) is a very common way to get a homogeneously suspension. The referred paper [6] describes the exact composition of a SDS suspension. The suspension was used to produce CNT covered PET by dip-coating and inkjet printing. The used suspension was matched to the experiments, which are used in this thesis. See section 4.2.2.

Electrophoresis is used to get CNTs on the tips for a scanning probe microscope [10]. Two razor blades were put together in a distance of 0.5 mm, facing the sharp sides. After this a suspension (isopropyl alcohol with MWCNTs) was put to the blades to cover them. An electric field (5 MHz AC voltage with $1.8 \text{ kV}\cdot\text{cm}^{-1}$) was applied on the blades in order to get the tubes align on the edges of the sharp sides. The blades were put on a moveable stage in a scanning electron microscope. After this a single CNT, which was lying on the blade's edge, was caught with a tip on the manipulator. In this theses the blades where changed to the tips itself, in order to get a single tube stuck on the top of the tip. See section 4.5.

4 Description of Processes

4.1 Scanning Electron Microscope

The carbon nano tubes are too small to be seen in a conventional optical microscopes because they are smaller as the light's wavelength. So a scanning electron microscope (SEM) was used for observation. In contrast to the optical microscope an electron beam scans the surface of a sample. Different kinds of electrons get reflected by the sample. The most used method is the secondary electron image mode. Therefore the secondary electrons get detected by a certain sensor in the SEM. High energy electrons enter the sample and scatter inelastically after a few nanometers on other electrons. Some of them, which are close to the surface, can escape from the sample and are collected by a detector [12]. A detailed description of SEMs is in the book *Physical Principles of Electron Microscopy* from Ray F. Egerton [13] pages 125 - 153.

A second mode for observation used in this thesis was the backscattered electron image method. Here the electrons were scattered elastically and got reflected. The secondary and the backscattered electrons can be differentiated by their kinetic energies. This method is used to visualize the chemical composition of the sample, because the elastic scattering is proportional to the charge of the atoms. So there is a strong atomic-number contrast [13]. Different materials have a different gray level.

Nearly all pictures, which are imaged in this thesis, are shot with the SEM (JEOL JSM - 6490LV). On every image in the left lower corner is the energy of the electron beam displayed (mostly 20 kV). The second number is the magnification, followed by the scale. The next is the working distance in millimeters, this is the distance from the end of the electron source to the surface of the sample. The spot size is described by a device specific number 50. The last figures show the detecting mode. SEI stands for secondary electrons and BEC for backscattered electrons.

For contact and mechanical measurements some manipulators are mounted in the vacuum chamber of the SEM. On top of these, measuring tips are fixed to contact to the sample's surfaces. The manipulators can be moved by piezoelectric materials in very slow steps.

4.2 Suspensions

In order to get single MWCNTs some suspensions were made. At first a suspension with deionised water was used, but that did not work because the CNTs are hydrophobic and they do not solve in water. So a solvent was needed. In some papers sodium dodecyl sulfate was used to get a suspension [6]. The ultrasonic treatment is applied to mixture the suspension and separate the clumps.

4.2.1 CNT with Water

- Suspension 1: 6 mg CNT in 20 ml deionised H₂O, ultrasonic bath for an hour
- Suspension 2: 4 mg CNT in 20 ml deionised H₂O, ultrasonic bath for an hour

4.2.2 CNT with SDS

Sodium dodecyl sulfate(SDS) is a common anionic surfactant for cleaning and hygiene products [11]. The SDS was bought from Sigma Aldrich.

- Suspension 3: 0.40 mg CNT in 40ml deionised H₂O with 4 mg of SDS, ultrasonic bath for 2 hours [6]
- Suspension 4: 2.5 mg CNT in 40ml deionised H₂O with 35 mg of SDS, ultrasonic bath for 2 hours

4.3 Coating and Casting Processes

4.3.1 Dip-Coating

Dip-coating is a process, where a sample is pulled out of a liquid very slowly, to get some material, which is solved or suspended in an aqueous solution, aligned on the surface of the sample. If the speed is slow enough, some crystals can be grown out with this process.

The slowest speed of the dip-coater, from SDI-Company Japan, is 10 nm/s. To guarantee a smooth and vibration free pulling of the tip, the dip-coater was mounted on a shock-absorbing table from HALCYONICS.

The used settings are listed in the table 2 below:

Table 2: Used Dip-Coating Settings

| Name | Speed / $\mu\text{m}\cdot\text{s}^{-1}$ | Number of Dipping | Time / h | Immersion Depth / mm |
|----------|---|-------------------|----------|----------------------|
| config 1 | 1 | 1x | 1.5 | 5 |
| config 2 | 2 | 5x | 1 | 1.5 |
| config 3 | 4 | 10x | 1 | 1.5 |
| config 4 | 0.1 | 1x | 13 | 5 |

4.3.2 Spin-Coating

For this process a drop of a suspension is put on a rotating silicon wafer in order to align single tubes on the surface in a small layer. The used rotation speed was 2000 rpm for 10 seconds.

4.3.3 Drop-Casting

For drop-casting, a drop of a suspension was put on silicon wafer, which was on a hotplate, to vaporise the liquid to align the suspended tubes on the surface.

4.4 Tip-making Processes

In order to experiment with platinum-iridium tips it was necessary to produce them. A former bachelor student found a way to make very sharp tips, which was the theme of his thesis. See section 2. Following the process steps are listed.

4.4.1 Spot Welding

The first step was to spot-weld the wire to a tungsten shaft with a of diameter 1 mm. Two different wires were used, gold (diameter: 0.025 mm) and platinum-iridium (diameter: 0.1 mm). In table 3 the spot-welding device settings are listed. The fixed wire was cut after some millimeters.

Table 3: Settings for PECO Spot-Welder

| Leistung - Power | Stromzeit Per. - Time of Current | sek. Spannung - secondary Voltage |
|------------------|----------------------------------|-----------------------------------|
| 2 | 2 | 2 |

4.4.2 Electrochemical Etching

The next step was the electrochemical etching. Therefore the shaft was mounted so that the top of the tip was dipping in an acid (Acetone + CaCl_2 and H_2O) just half of a millimeter or less. A graphite electrode was also dipped into this acid. The electrode and the shaft were connected to a source meter (KETHLEY 2636A). This device is software-controlled and so certain programs can be run. The used program applies an AC voltage and measures the current. The resistivity of this set-up is proportional to the sharpness of the tip. The sharper it is, the higher is the resistivity. This program stops the etching process when the current falls below a certain value. Every information about the software is found in the bachelor thesis [1]. After etching the tips were washed with deionised water in order to wash off the rest of the acid.

The etching produces very sharp tips with a diameter less than 100 nm. Problems appeared after some etching processes with the same acid. During the etching platinum-iridium was removed from the tip and the used acid was soiled. This changed the resistivity of the set-up and the tips were not sharpened enough.

This process produces a typical tip-shape, which is visible in figure 3.

4.4.3 Flame Annealing

After the electrochemical etching the tips were flame annealed. Therefore they were put into a flame of a Bunsen burner. The tip was put behind the blue part of the flame till it was glowing, which took about half a second up to one second. After this the tip was left to cool down outside the flame. This process was repeated 5 times. Afterwards the tip was washed again.

Based on annealing too long, the surface can get burned, melted and deformed.

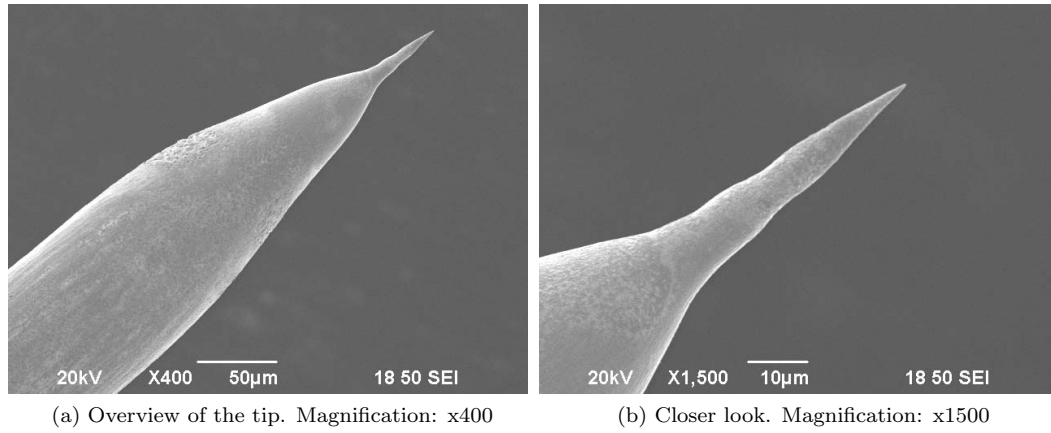


Figure 3: Typical shape of an etched platinum-iridium tip. The diameter of the top of the tip is less than a micrometer.

4.4.4 Micro-Polishing

The last step was the micro-polishing process. The tip got more sharpened with a second electrochemical etching method. A small gold ring was put into an acid ($\text{H}_2\text{SO}_4 \sim 1\%$) to wet the ring with a drop. The tip was mounted in an optical microscope so that the top of the tip touches the surface of the drop. Next the gold ring and the tip were connected to the ADWIN Pro 2. After that an AC voltage was applied with this device for 12 seconds. For information about the used configuration of the ADWIN see the thesis [1].

At the end 3 V were applied on the gold ring, ground on the tip, to remove the oxide, which was produced during all the processes before. The voltage should be applied for six minutes. After two weeks of using the same acid, the drop on the ring unstable and popped sometimes before the etching was finished. A new made acid helped to get a stable drop.

4.5 Electrophoresis

In a paper [10] the method of electrophoresis was used to get one CNT on the top of a tip. Two tips were mounted in a flat glass, so that the tops of the tips were facing each other. The distance was less than half a millimeter. After this a SDS suspension was filled in the glass to cover the tips. With the ADWIN a 500 kHz AC voltage (10 V maximum from ADWIN) was applied for a certain time. In order to affect the set-up as less as possible, it was waited for evaporation of the water. The original description in the paper was different, see section 3.4.

This method wasn't used that often because there was not enough time to perform and improve it.

5 Results

The used MWCNTs were bought from the company HIPCO. Macroscopically, they look like a black powder. The figure 4(a) shows this powder at a magnification of x140. The CNTs are stuck together to a big clump. At this magnification are no single tubes visible. To see them in the scanning electron microscope a magnification of x5000 is necessary (Figure 4(b)). In order to measure the resistivity, two of the manipulators were arranged to contact the clump, see figure 4(c). It was not possible to get one MWCNT on the tip. But a hole bundle stuck to the surface of the tungsten tip, figure 4(d).

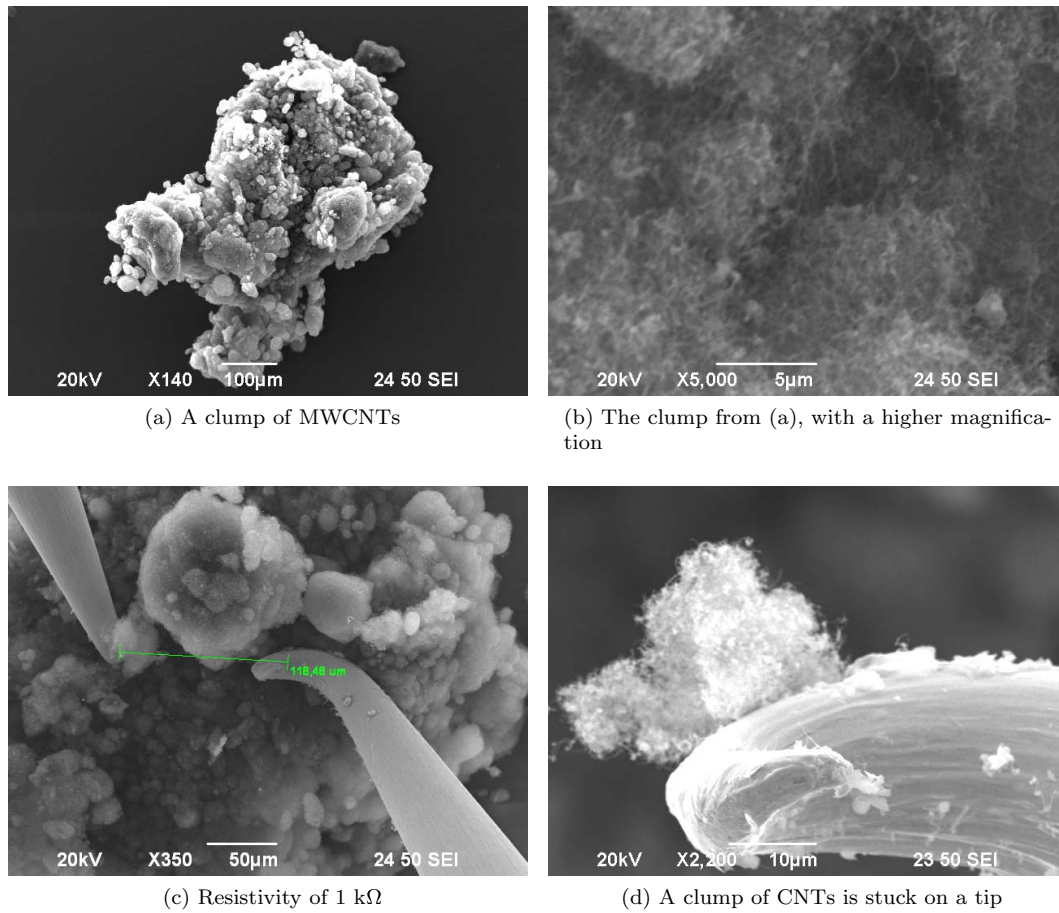


Figure 4: Clumps of CNTs.

The next step was to find a way to get single tubes. So a suspension (see section 4.2.1) with deionised water and CNTs was made. A drop of this suspension was put on a silicon wafer. After the water was evaporated the sample was observed in the SEM. Some single tubes were found, (see figure 5(a)) but it was not possible to get a single one stuck on the tip. Some mechanical experiments were made. By applying some force with the tips the clumps were deformed inelastically. Figure 5(c) shows this deformed clump. The CNTs did not stick to the silicon surface so it was possible to move them over the surface by pushing

them with the tips.

An experiment was made with a duck tape. A tungsten tip was put into this tape inside the SEM. After this it was tried to get a single tube stuck on the top of the tip. But it was not possible to catch one single CNT, just a smaller clump was pulled out from the bigger clump.

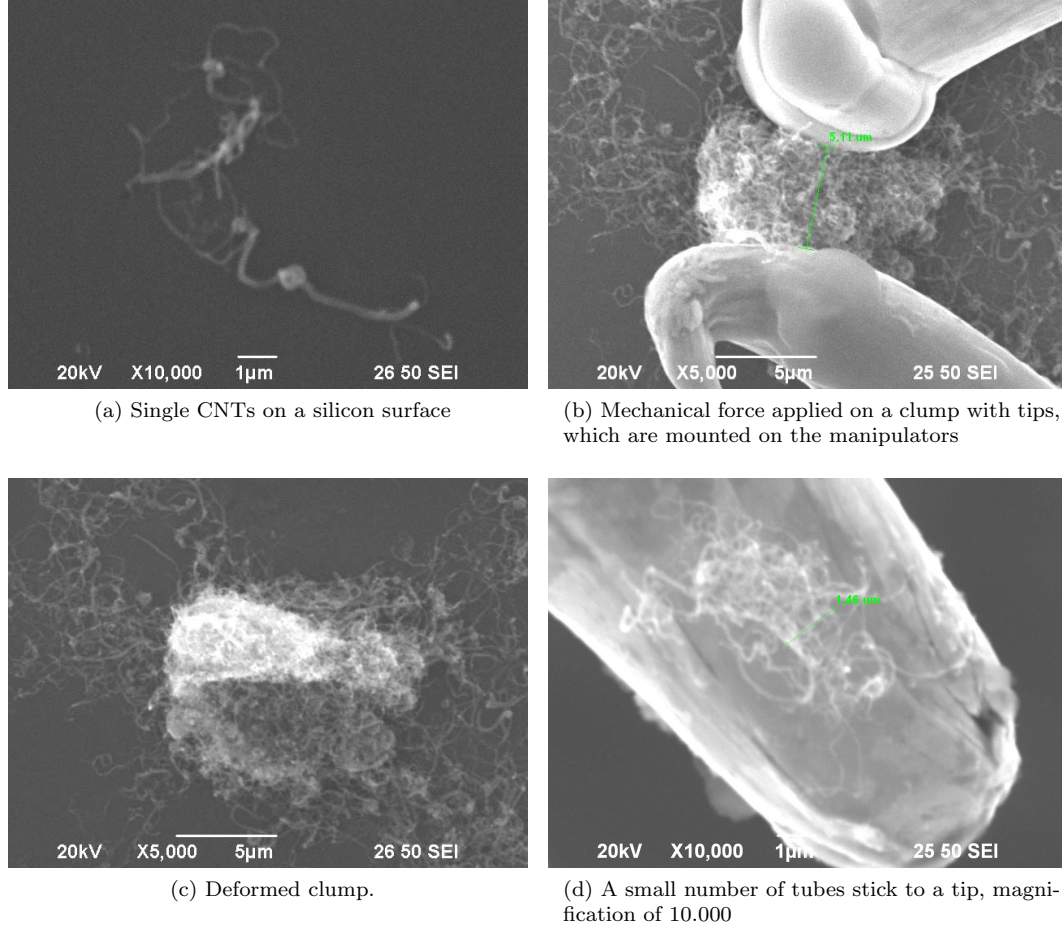


Figure 5: Single CNTs and clumps on silicon and on a tip

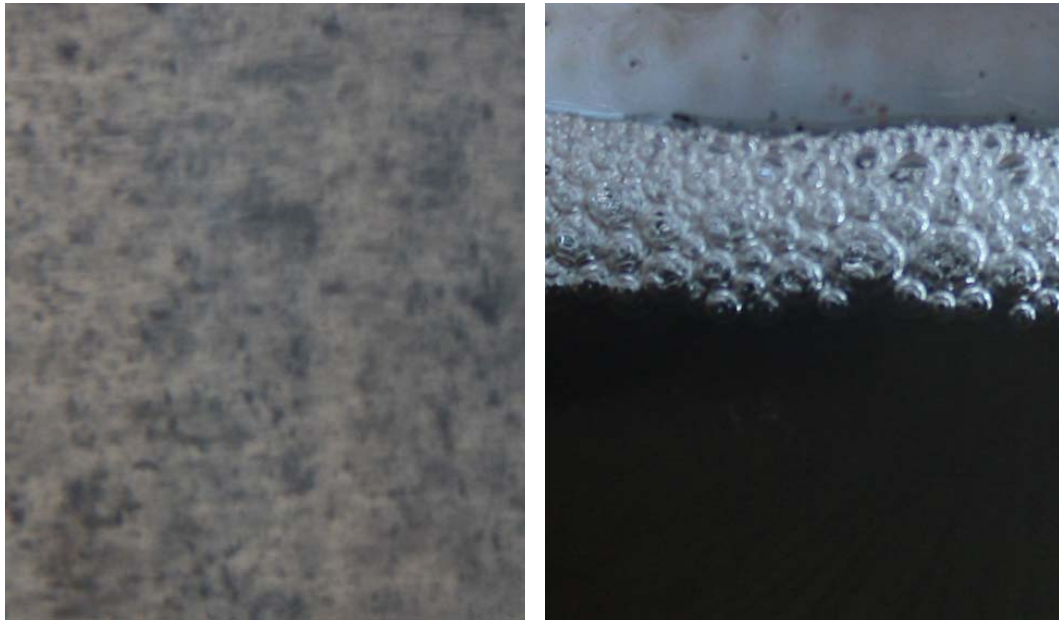
5.1 Dip-Coating

These experiments showed, that a suspension of tubes in water helped to get single tubes on a surface. So there must "swim" some single tubes and some bigger clumps. This is plausible because macroscopically are some small black partials swimming in the suspension, it is no homogeneous gray liquid. There was no significant macroscopic difference after longer treatment with ultrasonic.

In order to get a better suspension, sodium dodecyl sulfate (SDS) was used to suspend the tubes. See section 4.2.2 for an explanation for SDS. There was a significant macroscopic

difference between a suspension with and without SDS. In figure 6 the comparison is illustrated. To get some CNTs on the tip, they were dipped by hand into this suspension. The idea was, that the tubes align themselves in the pulling direction, because of the surface tensions of the liquid. But this method was ineffective. Pulling out the tip by hand was too quick and uncontrolled, so the method of dip-coating was used to optimize this process. For dip-coating see section 4.3.1.

A lot of different materials, solutions and dip-coater settings were tried to get the best results. In the following sections the results are listed:



(a) Suspension without SDS. Black particles are visible.

(b) Suspension with SDS. There is a homogeneous suspension.

Figure 6: Comparison between a suspension without and with SDS. The bubbles in (b) are produced by shaking the bottle.

5.1.1 Suspensions

The experiments showed that there are two ways how the CNTs stick to the surface, either as single tubes or as whole clumps. Although the suspension was treated with ultrasonic and SDS, there were still a lot of clumps in the suspensions. During the dip-coating the clumps stuck on the tip, independent from the location of the tip. Figure 7(b) shows a lot of clumps which are spread over the entire shaft. Sometimes a big clump stuck to the top of the tip and got formed by the surface tensions of the liquid. See figure 7(c) and (d).

Between all the clumps some single CNTs aligned on the surface. The concentration of these tubes depended on the time since the last ultrasonic treatment of the suspension, especially of suspension 1 and 2. The more time passed, the less single tubes stuck to the surface of the tip and the more clumps were caught. It might be that the CNTs clump again over time. The number of tubes became significantly smaller after one day without ultrasonic

treatment. These effects were not found at the beginning and caused several problems and a lot of experiments without CNTs on the tips. At first the reasons for the absence of the tubes were expected to be the surfaces, the materials and the dip-coating. Better results were achieved with ultrasonic treatment before every dip-coating process.

Another effect, which was useful to achieve bundles of nano tubes, is shown in figure 7 too. In some dip-coating experiments a small number of tubes aligned on sides of the top, see figure 7 (a). To improve this it was useful to dip-coat again. Several experiments showed that tubes mostly tend to stick to tubes than to the tip's surface. During the next dip-coating process the tubes stick to the existing tubes. Therefrom the idea of several times of dip-coating was concluded.

In some cases the entire tip was covered with a layer of tubes (with a thickness of a few micrometers) after a second dip-coating step. In the experiment (from figure 7) a bundle was produced.

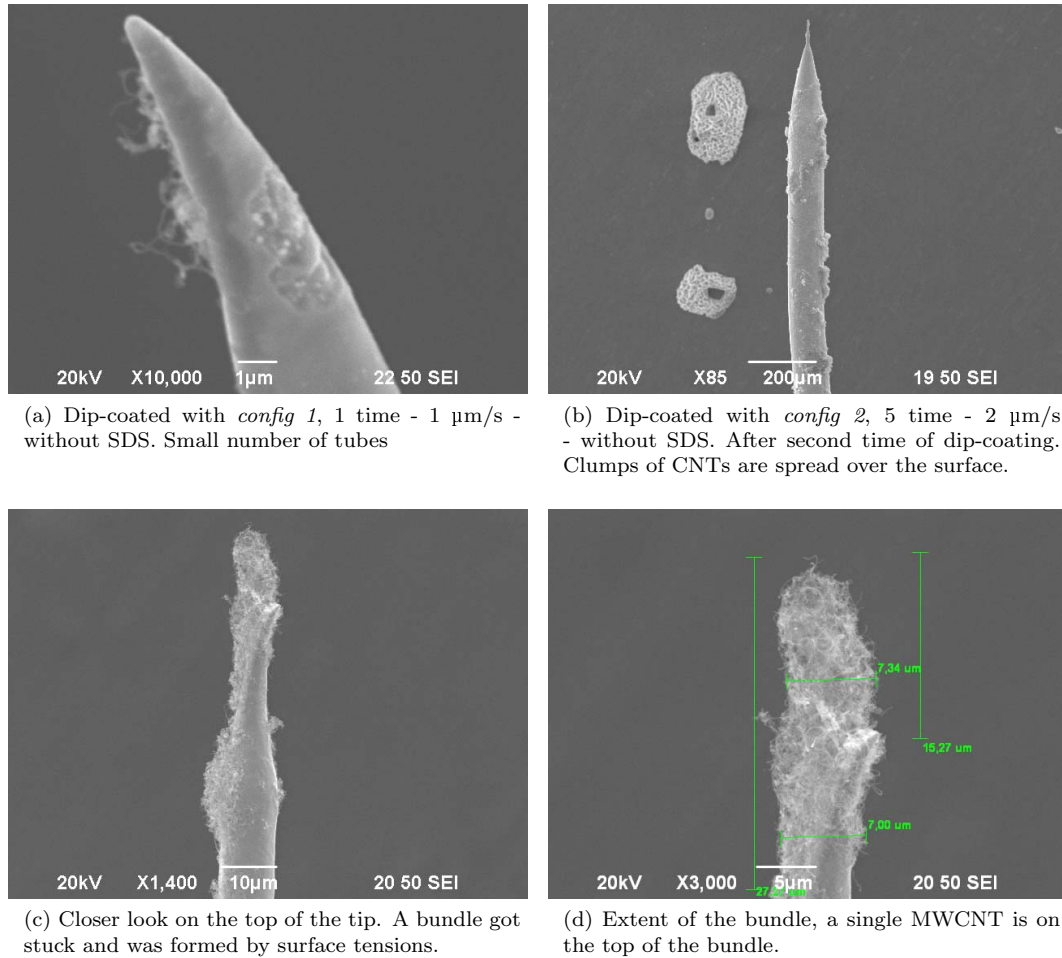


Figure 7: Platinum-iridium tip, all the pictures show the same tip. (a) once, (b), (c) and (d) twice dip-coated.

5.1.2 Material and Shape of the Tips

In order to make a contact to a surface and for exact navigation it is very useful to have a long, narrow, straight and sharp tip to get a good view at the surface under the tip and a small contact area. Considering these properties the tips were selected. Figure 8 shows some examples of suitable and unsuitable tips.

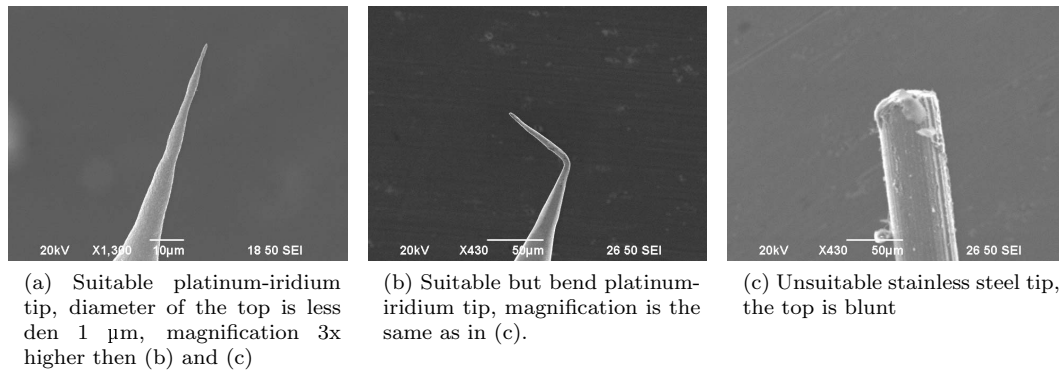


Figure 8: Suitable and unsuitable tips for measurements

To find out, which surface is the most qualified different, materials were tested.

- **Tungsten:**

The standard tungsten tips, which are bought from the company GGB-Industries, have a diameter between 1 μm to 2 μm . They are used for conventional experiments. Dip-coating showed that the CNTs stick to the tungsten surface. In comparison to platinum-iridium and gold, a lower dip-coating speed was necessary to achieve similar results. Figure 9(a) displays a tungsten tip with CNTs on it. A problem with tungsten was that sharp new tips were difficult to get and it was not possible to etch used and bend tips to sharpen them again (platinum-iridium etching method was tried, see section 4.4.2). In figure 9(b) a electrochemical etched tungsten is pictured, the etching changed the surface but the tip itself wasn't becoming sharper.

- **Platinum-Iridium:**

In contrast to the tungsten tips the platinum-iridium tips were not bought. The bachelor thesis of a former student was about producing these tips by etching and micro-polishing, for this bachelor thesis see section 2. To get platinum-iridium tips it was necessary to produce new tips. The process steps are listed in section 4.4. Platinum-iridium is suitable for dip-coating. The CNTs can stick to the surface and some good results were achieved. Figure 7 and 10 picture bundles of nano tubes on the top of platinum-iridium.

The aim of this bachelor thesis was to get a single MWCNT on the top of the tip. With the SDS-suspensions and platinum-iridium it was possible to realize this. See figure 11. For the contact measurement with this tip, see section 5.5.

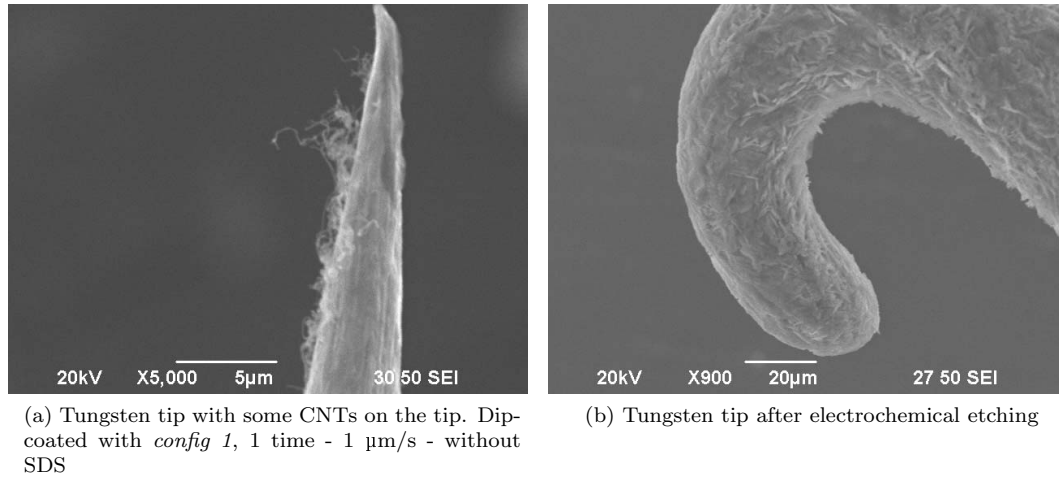


Figure 9: Tungsten tips

- **Gold:**

Similar to the platinum-iridium tips the gold tips were spot-welded. A wire with a diameter of 0.025 mm was fixed on a tungsten shaft, but it was not possible to etch gold electrochemically, see section 4.4.2. So the tips were not sharp enough to locate the contact area exactly.

The golden surface itself was perfectly qualified for the CNTs to stick on. A fast dip-coating speed produces (2 $\mu\text{m/s}$) tightly covered surfaces, see figure 12.

To get thin gold tips it was tried to put a small layer of gold (a few nano meters) on sharp platinum-iridium tips by evaporation of gold. It was also tried to fix a bundle of CNTs on the tip with this method, but it had no positive effects. Most of the tips were bend, burned or soiled. The process was time-consuming and the relation between used gold for evaporation and gold on the tips was unbalanced. This experiment is a waste of material.

The good adhesiveness of gold is due to the quality of this material. Gold does not form an oxide layer and pure metal surface might be more attractive than an oxide covered metal, like tungsten or platinum-iridium.

- **Graphite:**

A pencil lead from a mechanical pencil was used for dip-coating. The tubes align on the surface but it was not possible to make a sharp tip out of graphite. Besides, the pencil lead was not solid enough.

- **Silicon:**

The CNTs do not stick to the silicon surface, which was shown in the first experiments at the beginning. In a second test a silicon wafer was dip-coated after the surface was scratched with a diamond-scribe. But no tubes stick to the wafer, even in the rough scratches were no tubes.

A lot of different dip-coating times and speeds were tried. Generally the slower the speed the more tubes align on the tip. Configuration *config 3* (4 $\mu\text{m/s}$) was too fast, no tubes were

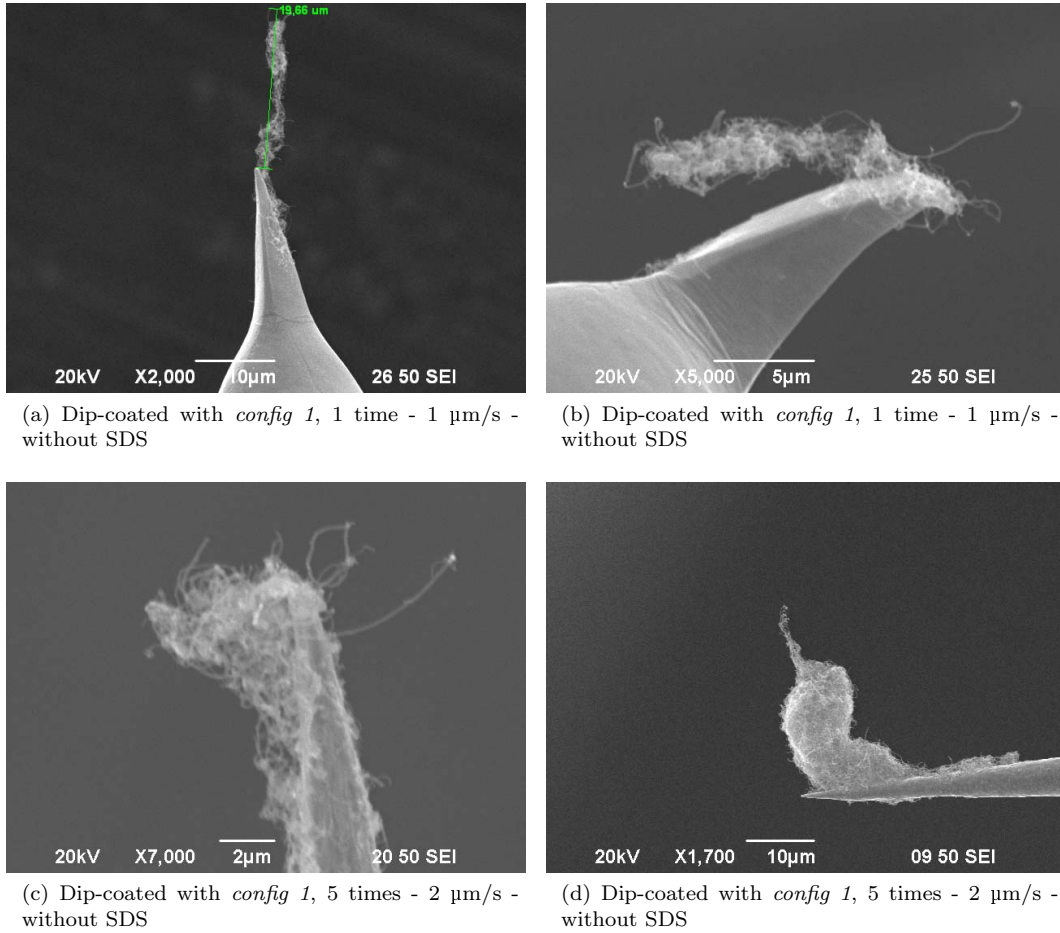


Figure 10: Examples of bundles on platinum-iridium tips.

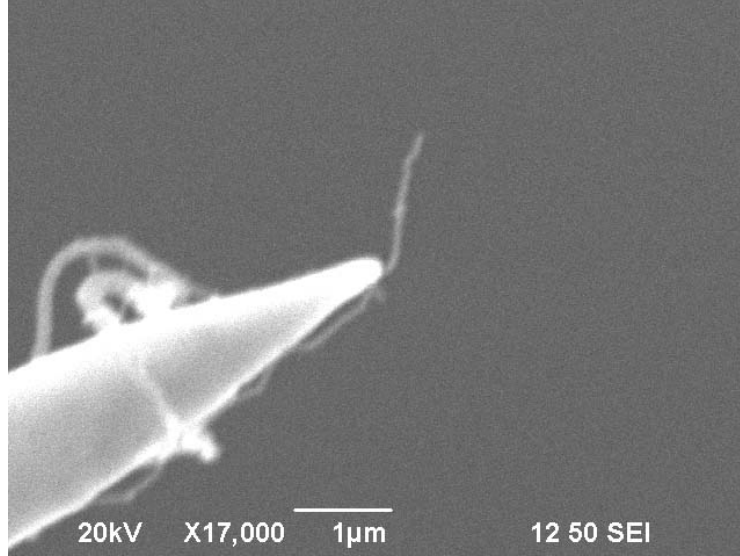
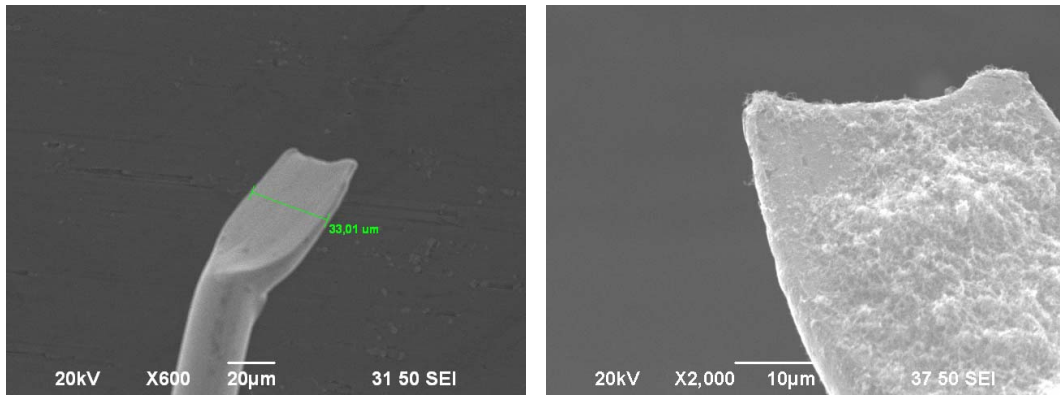


Figure 11: Single MWCNT on a platinum-iridium tip. Dip-coating settings *config 1*, 1 time - 1 $\mu\text{m/s}$ - with SDS - suspension 3



(a) Angular cut gold wire (diameter 0.025 mm)

(b) Gold tip after dip-coating, settings *config 1*, 1 time - 1 $\mu\text{m/s}$

Figure 12: Gold tip, before (a) and after dip-coating (b). The surface is closely covered with CNTs. Tip is not suitable for contact measurements because of its size, about 100 times to large.

found at this speed. The best results were achieved with a speed of 1 $\mu\text{m/s}$. A lower speed is not useful because the dip-coating time increases and less experiments can be realized. The 13 h tests (*config 4*) produced entire covered tips, which are not suited for exact electrical measurements.

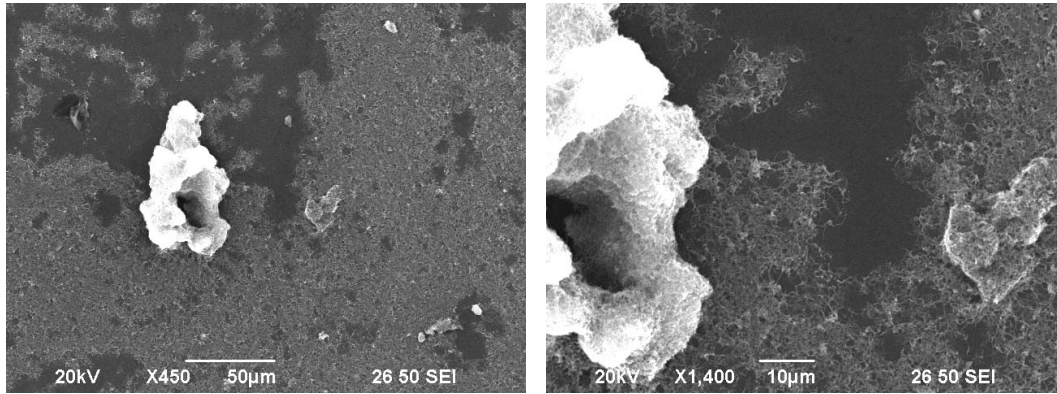
The amount of tubes per time is material depending, see the material specific points above.

5.2 Drop-Casting and Spin-Coating

The methods of drop-casting and spin-coating were used to examine the properties of the SDS-suspensions. For a detailed description of the processes see section 4.3.2 and 4.3.3.

The drop-casting experiments showed a difference between the SDS-suspensions and the water suspensions. There were less clumps of CNTs on the surfaces in the test with SDS than in the test without SDS. The drop-casting also produced a thin layer of CNTs in the center of the vaporized drop. See figure 13.

The spin-coating results surfaces with no layer and a small number of clumps. Most of the tubes get spun away by centrifugal force.



(a) White clump of CNTs and overview of the CNT's covered surface. Magnification: 450x

(b) Closer look, single CNTs are visible. Magnification: 1400x

Figure 13: Drop-coated silicon wafer.

5.3 Electrophoresis

The method of electrophoresis tries to get CNTs in a different way on the tips, see section 4.5. In figure 14 are two platinum-iridium tips visible. There is a significant difference to the dip-coated ones. By using the electrophoresis the tubes stuck much more to the surface than using dip-coating.

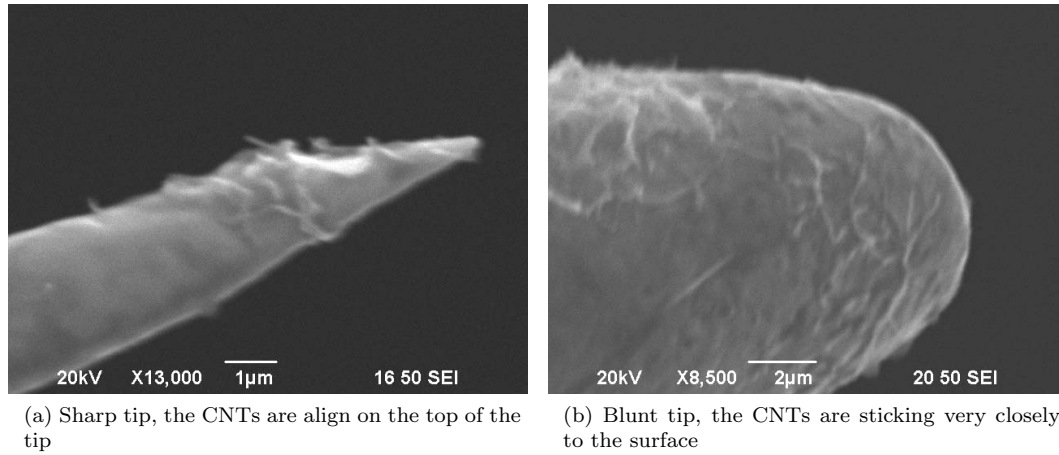


Figure 14: Platinum-iridium tips with some CNTs, fixed with electrophoresis. The AC voltage was applied for 10 minutes.

5.4 Effect of Used Processes on the Material Surfaces

Here are some observed material and surface effects listed. Some of them are resulted by tip making processes and some are caused by the dip-coating.

- **Surface Effects:**

In the following figures 15 the observed surface effects are pictured. In the captions the respective processes are listed, which concluded these results.

- **Deposits and Crystals:**

Not just the surfaces got influenced by the processes, even the suspensions and the CNTs were not pure and so some effects occurred. Figure 16 shows some grown crystals.

In some experiments some soil got stuck on the tips too. At first it is not always obvious if the soil is soil or a part of the material or the tubes. In figure 17(a) a bundle of tubes is displayed. The backscattered electron image (see section 4.1) shows the different materials in figure 17(b). The material, which is combined with the CNTs, is no metal backscattered electron images proves that there is some light material mixed to the CNTs.

5.5 Contact Measurements and Oxide

The adhesiveness of the CNTs to the tip (especially when they are formed to a bundle) is so strong that normal treatment, like evacuate the chamber, moving the manipulators even charring the tips around outside the vacuum, will not remove the CNTs. Mechanical forces like dropping the tip or pushing it against something deforms the bundles and removes some

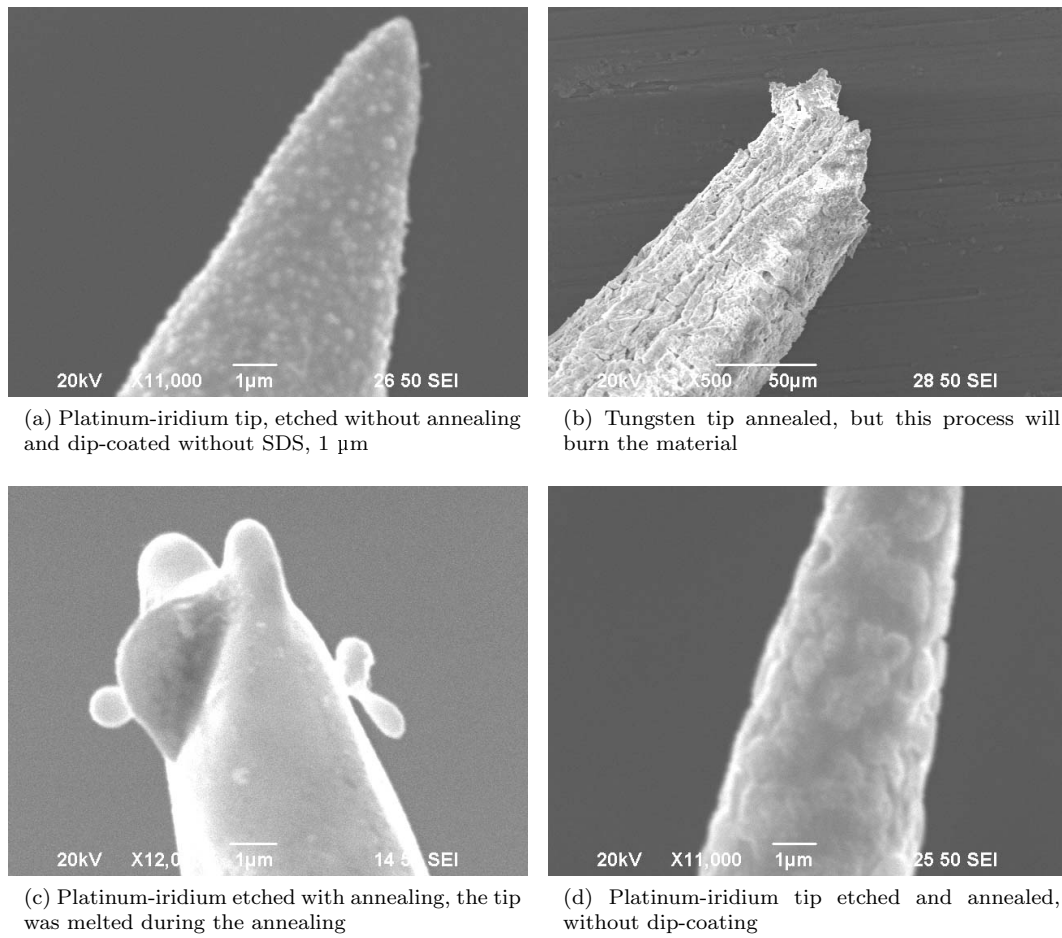


Figure 15: Observed surface effects

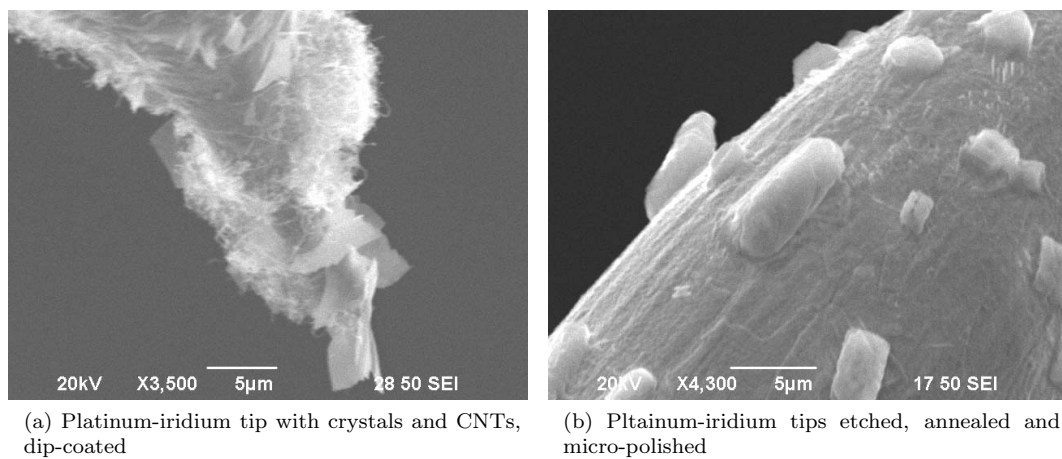


Figure 16: Observed crystals structures

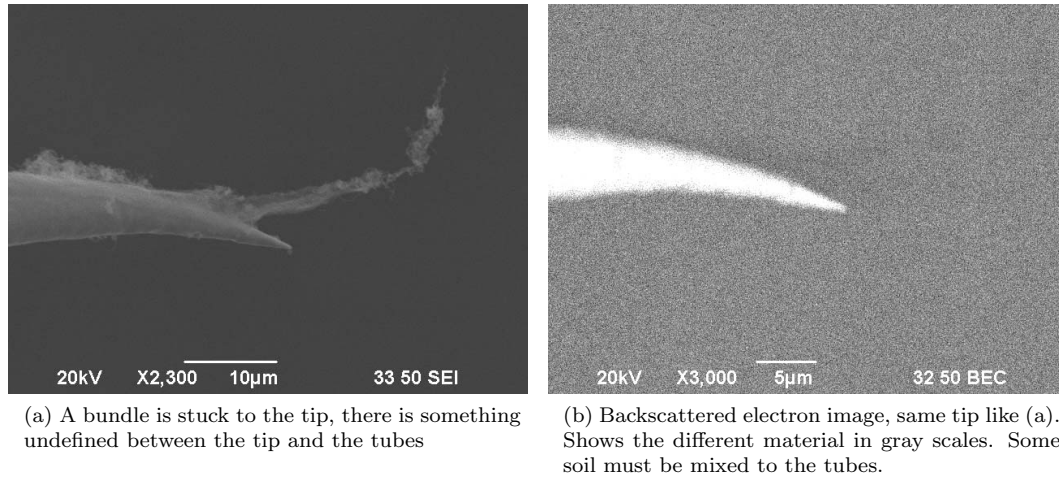


Figure 17: Soiled platinum-iridium tip in combination with CNTs

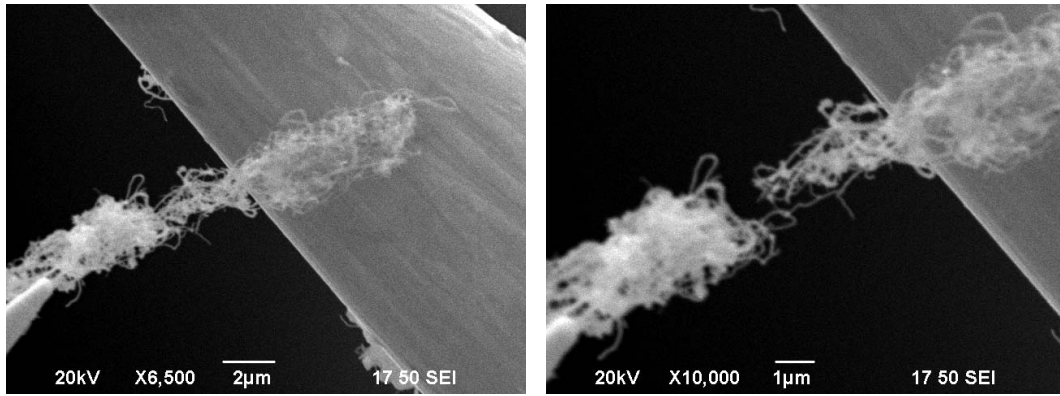
of the tubes.

For measurements the tips were mounted on the manipulators in the SEM. It was tried to make contact to several materials. In figure 18 the contact to a tungsten tip was made with a bundle of CNTs. The experiment showed (figure 18(a)) that the tubes rather stick to the tungsten than to itself, so the bundle broke while the tip was moved backwards. Just one tube was still connected to the bundle, see figure 18(b). For the bundle a resistivity of 33 k Ω was measured. Figure 18(c) shows an ohmic characteristic. The IV-characteristic (18) of the single MWCNT has a diode characteristic and the resistivity ranges from 1 to 9 M Ω . This high resistivity might be caused by a bad contact between the tubes. The move backwards might have had a bad influence on the contact between the surfaces and the bundle.

With the platinum-iridium tip from figure 10 contact measurements were made, see figure 19(a). During the mechanical experiments a video was made, see <http://www.youtube.com/watch?v=cf371Ed5Wfg>. It shows the mechanical properties of this MWCNT. It bent elastically and was strong enough to resist the upcoming forces.

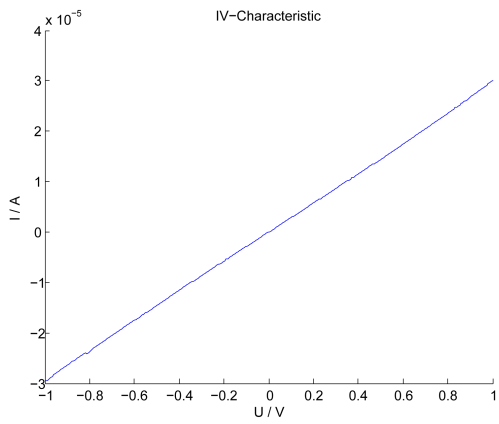
The problem was the electrical contact. For a short time electrical contact was established, although the MWCNT touched both surfaces. In order to measure something the whole tip was crashed on the surface and only after scratching on the surface a resistivity was measured, see figure 19(b). This tip was produced without the micro-polishing and oxide removal.

Some experiments with tips, which were produced without micro-polishing and oxide removal, showed that there are a general electrical contact problems. Therefore a platinum-iridium tip (shown in picture 20) was produced with all steps, which are listed in section 4.4. The contact measurement was made on a gold surface to exclude at least one oxide layer, the resistivity was 20 Ω .

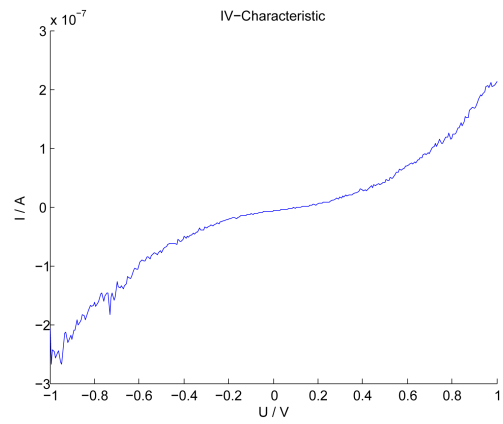


(a) The measured resistivity is in the range of $33 \text{ k}\Omega$

(b) The measured resistivity is in the range of several $\text{M}\Omega$



(c) IV-characteristic for the bundle of MWCNT in (a)



(d) IV-characteristic for the single MWCNT in (b)

Figure 18: Contact measurement with a bundle and a single MWCNT

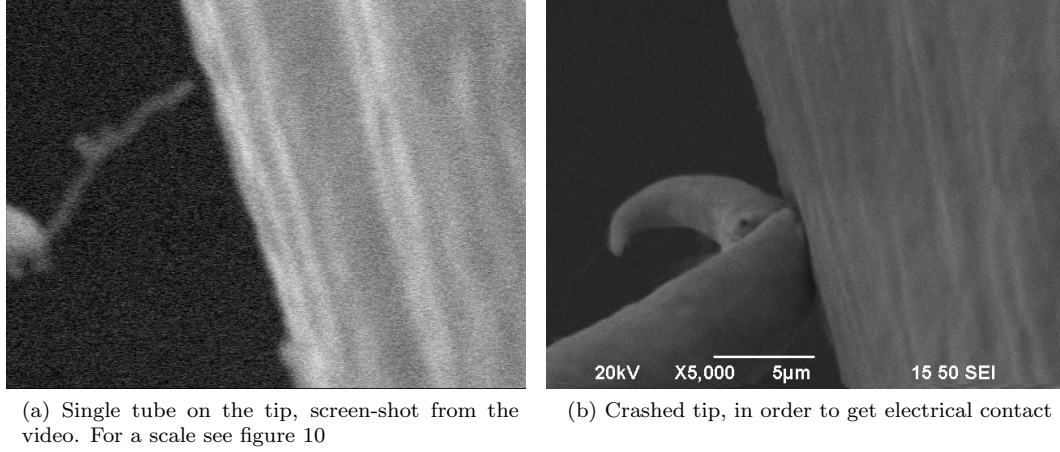


Figure 19: Single MWCNT contact measurement, platinum-iridium tip

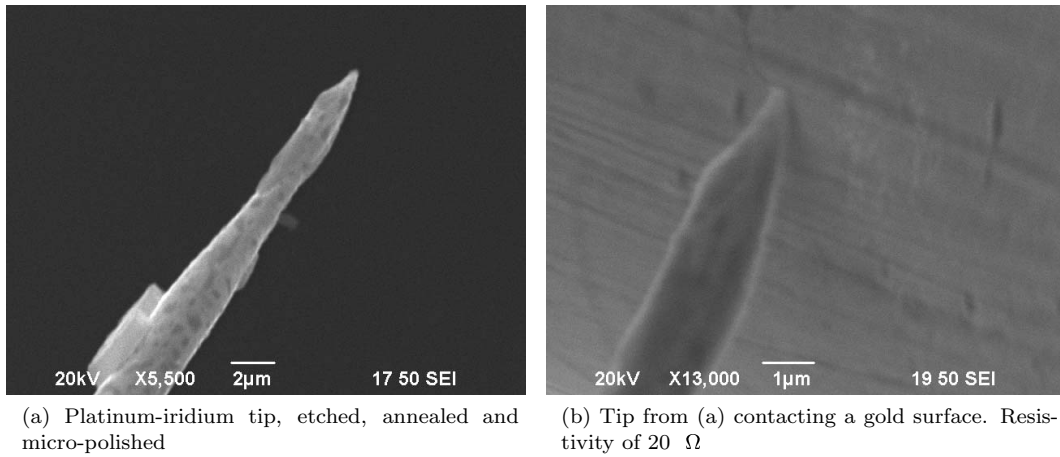


Figure 20: Micro-polished platinum-iridium tip

6 Conclusions

In the context of this thesis it was not possible to find a way to produce perfect CNT tips. But the experiments showed that in general it is possible. In some points success was achieved.

It is possible to get one single MWCNT on the tip, it is possible to have an elastic contact, the MWCNTs bend elastically and it is possible to measure current through a single MWCNT. Dip-coating was useful but hard to control. It is possible to work towards the wanted result but too many parameters had an influence and so the result was not predictable. The suspension was the biggest problem. SDS helped but there were still too many clumps in the liquid to get a reproduce able amount of tubes on the tip. It was necessary to treat the suspensions with ultrasonic before every dip-coating process to get at least a better suspension.

Basically gold is the best material for dip-coating, but the used gold wire was not etch-able so the tips were not sharp enough. Dip-coating is always a risk of destroying the tip's surface and so it is a waste to use new bought tungsten tips. There was also no way to sharpen used tips. The best tips were made with platinum-iridium, but this material is forming an oxide on its surface. In general for dip-coating the shape of the tip is much more important than the material. In contrast to the conductivity. The oxide has an big influence on the results. A single MWCNT on the tip has no sense when an oxide layer interrupts the electrical conductivity. From this angle gold would be the best material. Some ideas, how to fix this dilemma, are described in the next section.

There was not enough time to figure out if the oxide was formed by the dip-coating process and if the micro-polishing helps to get electrical contact through CNTs.

If the problems, listed above are solved, the actual measurement is no big problem. The adhesive forces between the tube and the tip's surface is strong enough to resist the forces and the tube bend elastically. Not each bundle is flexible but the single tubes are. Also the contact to a silicon surface is easily because the tubes do not stick to the silicon.

The method of electrophoresis was used twice because there was not enough time. This has to be optimised, but there is a lot of potential. Especially because the tubes seem to stick much closer to the surfaces. But the influence of electrophoresis on the surfaces was not clarified.

In general it is possible to achieve the aim of this thesis but the time of three weeks in the laboratory was too short to find a perfect and reproduceable way to get such tips.

7 List of Suggestions

This thesis covers a lot of ideas and processes. While working in the laboratory and writing this thesis, improvements and new ideas came up. The following list displays the most relevant ideas, questions and suggestions to improve the used methods and motivate further research.

- More experiments with micro-polished tips should be made to find out if the dip-coating produces an oxide layer on micro-polished tips.
- The platinum-iridium tips should be plated with gold by electroplating. This would improve the dip-coating and would solve the problem of oxide formation.
- A way to etch gold electrochemical should be found to get suitable shaped gold tips for dip-coating to prevent oxide formation.
- The suspensions should be improved with a stronger ultrasonic device and a method to filter the bigger clumps from the suspensions.
- Longer and straighter MWCNTs should be used for all the experiments.
- The method of electrophoresis has potential. More experiments should be made with different kind of suspensions, for example isopropyl alcohol with MWCNTs. The used liquid should be vaporised more quickly.

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