

TMM4910  
Integrity of constructions  
Surface structuring with carbon nanotubes

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## **Abstract**

Carbon nanotubes is of great research interest since they are one of the most versatile materials in the world. The full potential is not yet known since creating huge amount of defect free CNTs for industrial application is still not yet reached, but many of the carbon nanotubes incredible properties are known. The CNTs strength, electrical and thermal properties are looked at together with the most known and used methods for producing carbon nanotubes. Experiments conducted at NTNU NanoLab are explained and presented.

Karbon nanorør er under stor forskningsinteresse siden de er en av de mest versatile materialene i verden. Det fulle potensialet er enda ikke funnet siden det å produsere store mengder defektfrie karbon nanorør for industriell bruk er enda ikke nådd, men mange av karbon nanorørets fantastiske egenskaper er kjent. Karbon nanorørets styrke, elektriske og termiske egenskaper er sett på sammen med de mest kjente og brukte metodene for karbon nanorør produksjon. Eksperimenter utført ved NTNU NanoLab er forklart og presentert.

## Preface

This report concludes the work done in the course TMM4910 (30 credits), Integrity of constructions, Surface structuring with carbon nanotubes. This report is written to present the literature study and the experiments done at the NTNU NanoLab for the Master thesis “Surface structuring with carbon nanotubes” done by Eirik Stavik Rønning during the spring of 2011. Eirik Stavik Rønning belongs to the study program I&IKT, with specialization in product development and materials at IPM.

I would like to thank my Professor Christian Thaulow for the support and interest for the subject and the experiments done at the NTNU NanoLab, Espen Rognstad for taking the time to help me out so much with the PECVD and recipes and Øystein Dahl for some great input regarding the experiments.

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# 1 Introduction

Carbon nanotubes have created interest since the day they have been discovered. They are one of the most versatile materials known thus far with their great strength, high modulus, electrical and thermal properties. There are many potential usages for carbon nanotubes, but also many obstacles to overcome so that they can be used to their full potential. Much research is done in the field both to find scalable methods to produce defect free SWNT and MWNT and usages for them.

This Master thesis looks at some of the properties and the most used fabrication methods of CNTs. It also contains own experiments done at the NTNU NanoLab where growth of CNTs directly on steel surfaces with PECVD was explored. All experiments were done with PECVD at NTNU NanoLab.

## 2 Carbon Nanotubes

Carbon nanotubes was discovered in 1991 by Suimo Iijima [1]. The carbon nanotubes was created by the carbon-arc discharge method which was similar to the method used for fullerenes preparation. To observe the carbon nanotubes in high resolution Suimo Iijima used high resolution transmission electron microscopy. The observations Suimo Iijima made were of multi-walled carbon nanotubes.

The first observation of singel-walled carbon nanotubes were made 2 years later by Suimo Iijima and Toshinari Ichihashi [2]. To create the single-walled carbon nanotube they used carbon electrodes with a small piece of iron and filled the the chamber with aragon and and methane gas.

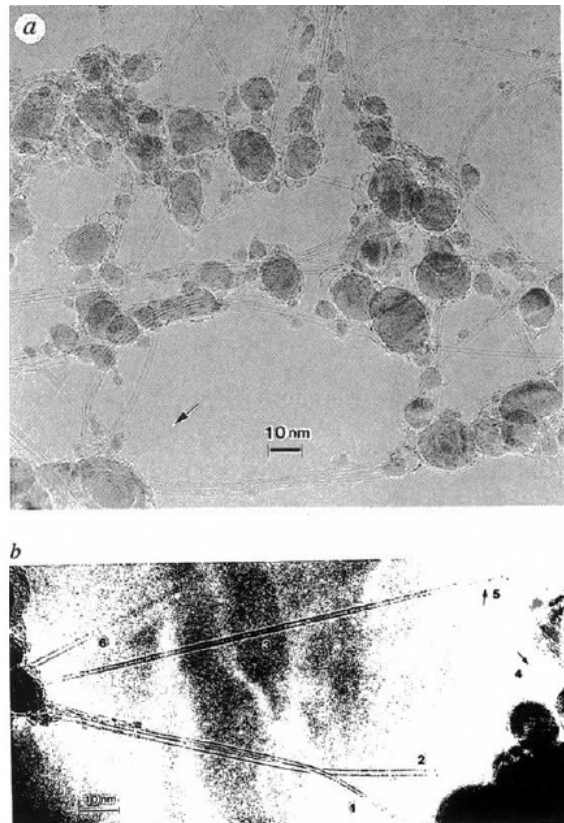


Figure 1: Electron micrograph of single shelled carbon nanotubes found by Sumio Iijima & Toshinari Ichihashi [2].

The name carbon nanotube comes from their size, wich is only a few nanometers wide. Carbon nanotubes are by definition carbon molecules which is cylindrically arranged. They have properties that can make them extremely useful in electronics and mechanical applications.

## 2.1 Structure

Single-walled carbon nanotubes(SWNT) usually have a diameter about 1nm, the length can vary extremely and be up to million times longer. The structure of a SWNT is made up from a single graphene sheet, which is a one layer thick graphine sheet, that is rolled seamlessly. Depending on how the carbon nanotube wall is rolled together from the graphene sheet the walls can end up in an armchair, zigzag or chiral shape(Fig.2).

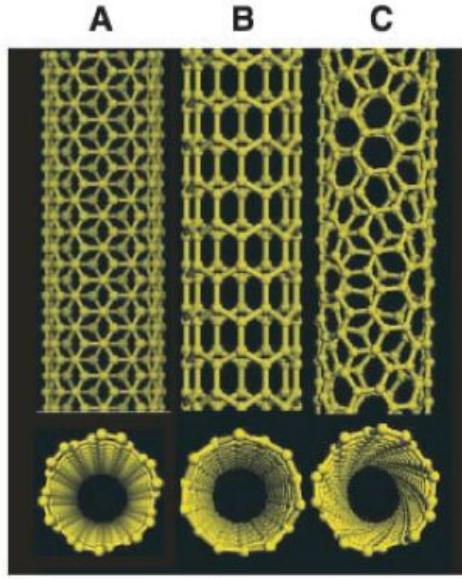


Figure 2: Structures of the single-walled carbon nanotube. (A) armchair, (B) zigzag and (C) chiral [3].

$C_h = n\hat{a}_1 + m\hat{a}_2$  is the equation for the chiral vector, where  $\hat{a}_1$  and  $\hat{a}_2$  are unit vectors in the two dimensional honeycomb crystal lattice and  $n$  and  $m$  are integers. The chiral vector determines the unit cells which is what distinguish the different structures. The chiral angle is another important parameter, this is the angle between  $C_h$  and  $\hat{a}_1$ . If  $n = m$ , the chiral angle is  $30^\circ$ , we get the armchair sctructure(Fig.3). If  $n$  or  $m$  are zero and the chiral angle is zero, we get the zigzag structure. We get the chiral nanotube structure when the chiral angle is between  $0^\circ$  and  $30^\circ$ .

The ideal diameter of a SWNT is found by the equation [5]:

$$d = \frac{a}{\pi} \sqrt{(n^2 + nm + m^2)} \quad (2.1.1)$$

where  $a = 0.246$  nm.

The properties of single-walled carbon nanotubes change significantly depending on the  $n$  and  $m$  values. Most significantly their band gap can vary between 0.0eV to around 2.0eV. When the band gap is 0.0eV the nanotube

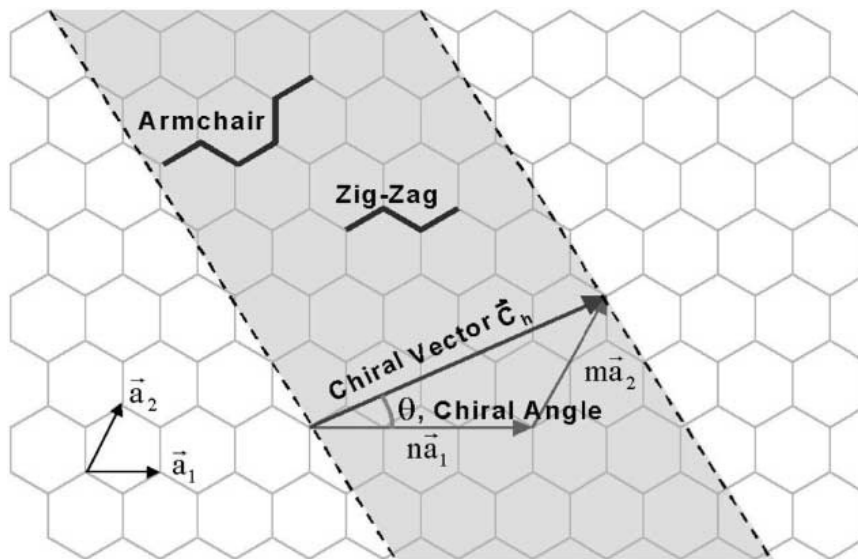


Figure 3: How a sheet of graphene is rolled up to form a carbon nanotube [4].

acts metallic. This only happens when  $n = m$ , that is with the armchair structure. With the zigzag,  $n - m = 3L$ , are semiconductors with a tiny band gap. All other variations are semiconductors where the band gap depends on the diameter [5] [6].

Multi-walled carbon nanotubes(MWNT) are made up from multiple rolled layers of graphite(Fig.4). There are two different ways to describe the way the nanotubes are rolled up. If you have a sheets of cocentric cylinders, for example a single-walled carbon nanotube inside a larger single-walled carbon nanotube, it's called the Russian Doll model. In the Parchment model, you have a single sheet of graphite that is rolled together like a parchment [5]. The diameter is usually between 2 and 25nm and the distance between the graphite sheets is about  $34\text{\AA}$  [7].

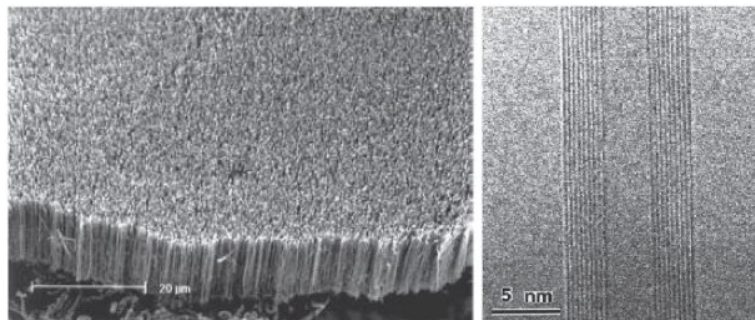


Figure 4: To the left we see a scanning electron microscope(SEM) image for an MWNT forest. The picture on the left is a MWNT consisting of nine SWNTs taken with a TEM [3].



## 2.2 Properties

Since the discovery of carbon nanotubes many researchers have focused on carbon nanotubes. The properties reported for carbon nanotubes are remarkable but physical and mechanical. The tensile strength and elastic modulus of carbon nanotubes are the highest of any materials yet discovered. Carbon nanotubes also have unique electrical properties and have an extreme thermal capability.

### 2.2.1 Strength

The strength of the carbon nanotubes comes from the covalent  $sp^2$  between the carbon atoms. In 2000 Min-Feng Yu *et al.* measured the tensile strength for MWNT with a “nanostressing device” (Fig.5) that was located inside a SEM. The tensile stress recorded for the outermost layer of the MWNT was recorded between 19 and 63 GPa. They also reported that the Young’s Modulus, E, for the outermost layer varied between 270 to 950 GPa after analysing their stress-strain curves [8].

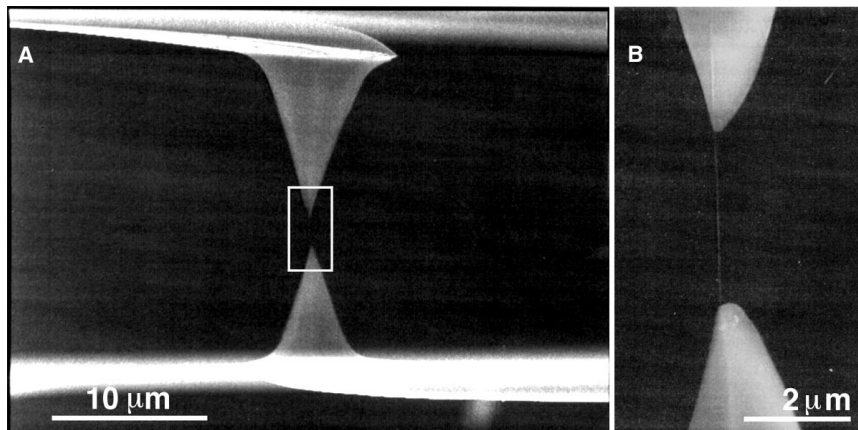


Figure 5: The “nanostressing device” used by Min-Feng Yu *et al.* (A) MWNT mounted between to tips of a AFM. (B) Magnification of the highlighted area in (A) [8].

In 2008 Bei Peng *et al.* reported multiwalled carbon-nanotubes with a mean fracture strength of  $>100\text{GPa}$ . This is three times the fractures strength of earlier observations. To get this performance they omitted chemical treatments from the sample premaration process. By doing this they avoided the formation of defects. Thier results corresponds excellent with quantum-mechanical estimates for nanotubeswith containing few defects. They are  $\sim 80\%$  of the expected for defect free tubes [9].

### 2.2.2 Electrical

Single-walled metallic carbon nanotubes have in theory excellent electrical properties. They have a carrier mobility of  $10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is better than silicon. They can carry an electrical current density of  $4 \times 10^9 \text{ A cm}^2$  which is more than 1000 that of conventional metals like copper or aluminum [10].

### 2.2.3 Thermal

Single-walled carbon nanotubes shows great thermal conductivity. Measurements have shown that SWNTs has a conductivity of  $3500 \text{ Wm}^{-1}\text{K}^{-1}$  along its axis and a conductivity of  $1.52 \text{ Wm}^{-1}\text{K}^{-1}$  across it's axis. The thermal conductivity along the SWNTs axis is almost 10 times that of copper,  $385 \text{ Wm}^{-1}\text{K}^{-1}$ , which is know for its good thermal conductivity. Theory predicts an extremely high thermal conductivity value ( $6000 \text{ Wm}^{-1}\text{K}^{-1}$ ) of an isolated SWNT at room temperatureciteMJBiercuk.

M. J. Biercuk *et al.* used single-walled carbon nanotubes to augment the thermal transport properties of industrial epoxy. They created epoxy composites that was loaded with raw SWNT soot, grown by a HiPCO (high pressure carbon monoxide) method and epoxy composites with vapor grown carbon fibers (VGCF). They measured thermal conductivity enhancement of SWNT-epoxy composites greater than 125% with 1.0 wt% loading. For 1.0 wt% the VGCF-composite showed only an enhancement of 45%. Fig.6 shows room temperature data as a function of carbon loading. The electrical conductivity for the SWNT-epoxy rose sharply by nearly  $10^5$  between 0.1 and 0.2 wt% SWNT load, and not before 1 - 2 wt% for VGCF-composites citeMJBiercuk.

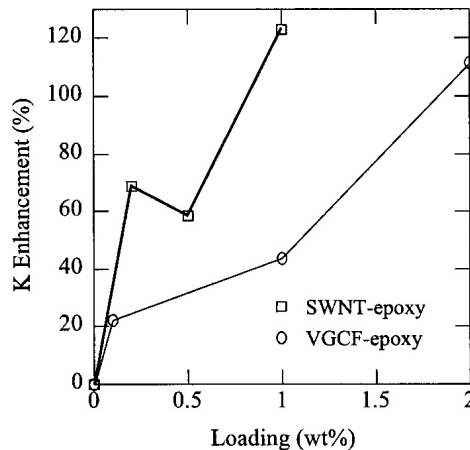


Figure 6: Thermal conductivity enhancement relative to pristine epoxy as a function of SWNT and VGCF loading [11].

## 2.3 Fabrication methods

There is several different methods to fabricate carbon nanotubes. The carbon nanotube structures are formed in essentially the same way, but the methods are different. The methods presented here are the most known methods to create carbon nanotubes, either SWNT or MWNT. Most of the processes grow the carbon nanotubes in vacuum or with process gasses. Growing carbon nanotubes with CVD can happen in both vacuum or atmospheric pressure.

### 2.3.1 Arc discharge

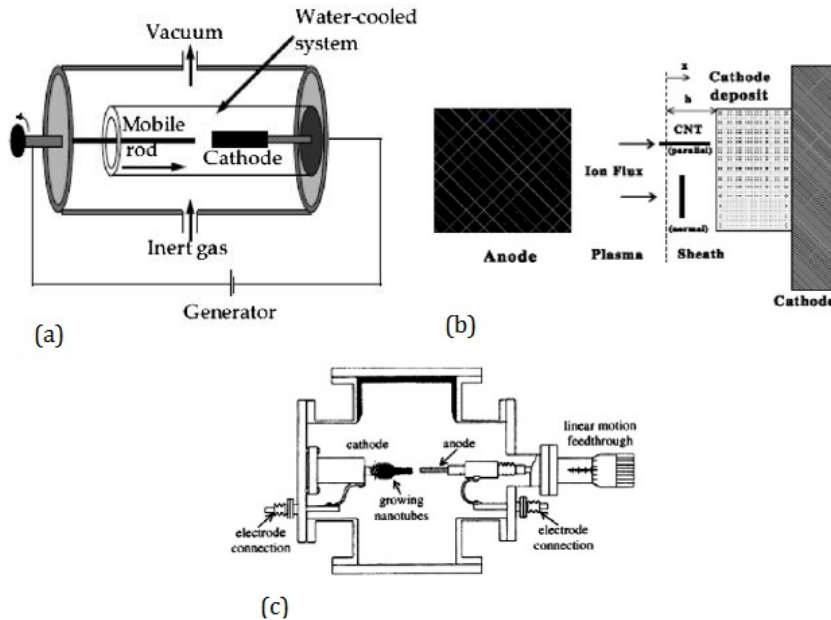


Figure 7: (a) Illustration of a electric-arc method. (b) Arc-discharge and CNT formation. (c) Illustration of Arc-discharge method [6].

It was with the arc method carbon nanotubes were discovered [1]. The arc method uses low pressure He or another neutral atmospheres. Fig.7(a) illustrates the arc discharge chamber. The most common arc discharge method used is the electric arc discharge method. In this method an electric arc discharge is generated between two electrodes made of graphite in an atmosphere of either Argon or Helium (Fig.7(b - c)). The typical yield for the arc discharge method is 30% by weight and produces both multi-walled and single-walled carbon nanotubes with few defects. The length of the carbon nanotubes are up to  $50\mu\text{m}$  and they are deposited in random directions and sizes [12].

C. Journet *et al.* used an electric arc technique that generated large quantities of single-walled carbon nanotubes. Their discharge was between graphite electrodes in a helium atmosphere. They drilled a hole in the anode which they filled with a mixture of graphite powder and metallic catalysts. The catalyst they got the best result with was a mixture of 1 atomic percent(at.%) of Yttrium and 4.2 atomic percent of Nickel. Fig.8 shows a bundle of entangled carbon nanotube filaments they observed with a SEM. The diameters of the carbon nanotubes are about 1.4nm. These bundles were homogeneously distributed over large areas and the distance between each bundle was several microns [13].

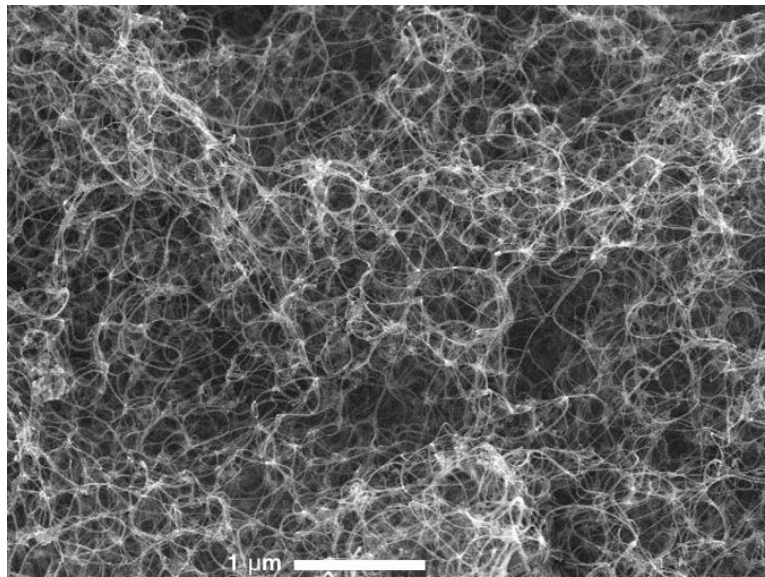


Figure 8: A SEM image of the material that was formed around the cathode, showing a high density of entangled carbon nanotubes [13]

J.L. Hutchison *et al.* fabricated double-walled carbon nanotubes by using a hydrogen arc discharge method in an atmosphere of hydrogen and argon (1:1 ratio) at 350 Torr with a 410-Torr partial vacuum. Both the anode and cathode was graphite. They drilled a channel in the anode to put the catalyst in, which was a mixture of 2.6 Ni, Co 0.7, Fe 1.45 and S 0.75 at.%. The process duration was about 40 min. To observe the DWNT they used high resolution electron microscopy (HREM)(Fig.9). [14].

Toshiki Sugai *et al.* presented a synthesis to create high-quality double-walled carbon nanotube by using a high-temperature pulsed arc discharge method at 1250°C. Both electrodes were graphite, which were doped with catalyst materials (Ni/Co 0.7/0.7 at. % and Y/Ni 1.0/4.2 at. %). The arc discharge were carried out in a high-temperature Argon buffer gas. To observe the DWNT they used transmission electron microscopy (TEM)(Fig.10)

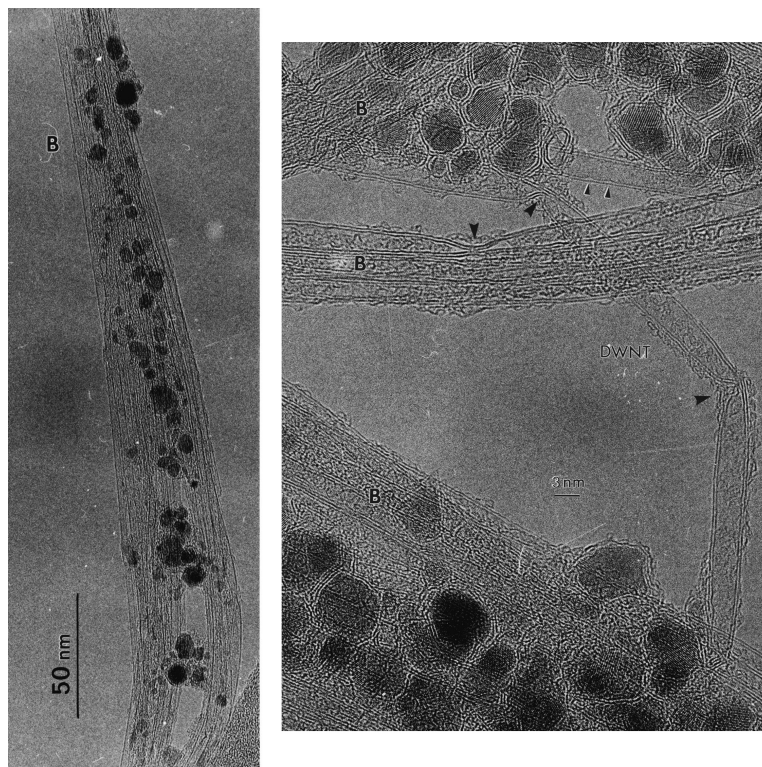


Figure 9: Showing bundles (B) and separate double-walled carbon nanotubes. Large arrows shows regions of DWNT disortions. Small arrows shows small local variations of nanotube diameter [14].

and Raman spectroscopy. The observed inner and outer diameter of the double-walled carbon nanotubes were 0.8-1.2 and 1.6-2.0 nm, respectively [15].

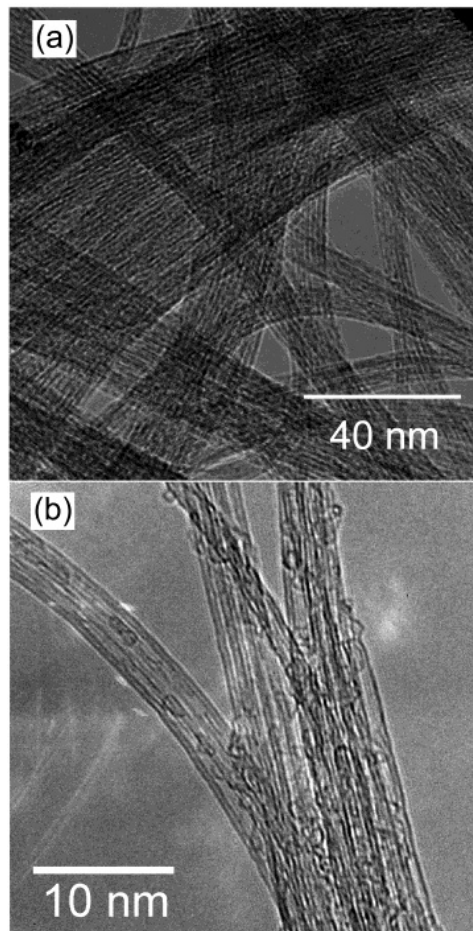


Figure 10: TEM image of the bundles (a) and double-walled carbon nanotubes (b) by the high-temperature pulsed arc discharge[15].

### 2.3.2 Laser ablation

In the laser ablation process a piece of graphite is vaporized by a pulsed laser under an inert atmosphere in a high temperature chamber. When the vaporized graphite condenses it produces soot which contains carbon nanotubes [6]. This process can produce both single-walled and multi-walled carbon nanotubes, but it is primarily used to create single-walled carbon nanotubes. The yield for the laser ablation method is around 70%, but it is also the most costly. The diameter of the carbon nanotubes produced by laser ablation can be controlled by the reaction temperature. This process was developed by Richard Smalley and his co-workers at Rice University, where they blasted metal with laser to produce fancier metal molecules, when they heard of the discovery of carbon nanotubes. They switched out the metal with graphite as was soon able to produce carbon nanotubes on their own [5] [12].

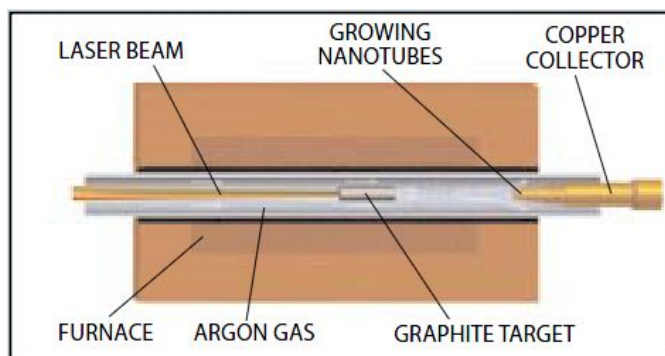


Figure 11: Laser ablation process [12].

Y. Zhang *et al.* synthesized single-walled carbon nanotubes in a nitrogen atmosphere and studied the results in a transmission electron microscope and electron energy-loss spectroscopy. The experiment was carried out in an electrical tube furnace which were heated to 1200°C and nitrogen was used as a carrier gas. The laser pulse was directed to the surface of the target and was focused to get an energy density of  $3\text{J}/\text{cm}^2$  per pulse. To synthesize the single-walled carbon nanotubes a graphite target containing 1.2 at.% (Ni + Co) was used. Most of the SWNTs had a diameter of 1.3-1.4 nm. TEM imaging shows in Fig.12(a) dark metal particles dispersed in the amorphous carbon, Fig. 12(b) a bundle about 30nm in diameter and in Fig.12 some small bundles and individual single-walled carbon nanotubes [16].

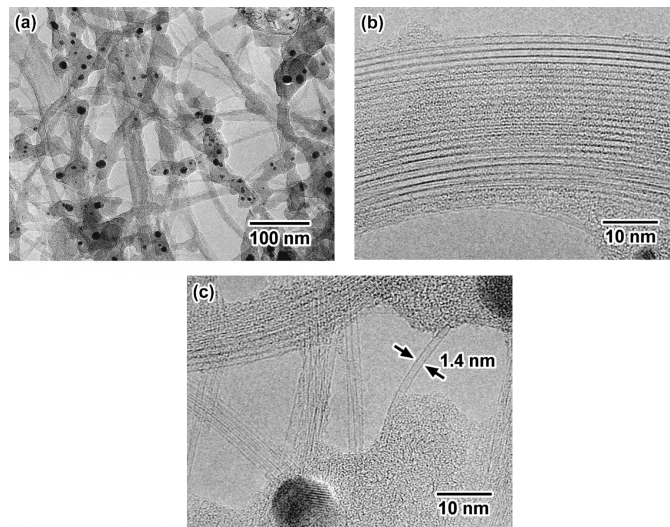


Figure 12: (a) TEM imaging of the laser ablation products, which shows high yield of SWNT. (b) A TEM image of a 30nm bundle with a diameter of 30nm. (c) Small bundles of SWNTs and single nanotube with a diameter about 1.4nm [16]

### 2.3.3 CVD

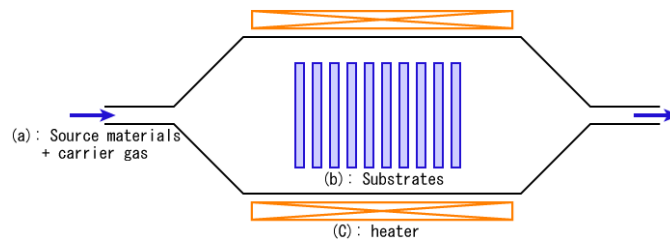


Figure 13: Illustration of a Thermal CVD furnace [17].

The most common method to create carbon nanotubes is the chemical vapor deposition (CVD) of hydrocarbon gases. The process involves heating a catalyst material to high temperatures, about  $500^{\circ}\text{C}$  -  $1000^{\circ}\text{C}$ , in a tube furnace and then flow a hydrocarbon gas into the furnace over a period of time. At the sites of the catalyst the hydrocarbon gas will break apart and the carbon is transported to the edge of the catalyst particle and start forming the carbon nanotube. The catalyst particle is either at the top of the growing nanotube under the process or at the base. The type of nanotubes you get depends on which catalyst that is used. Multi-walled carbon nanotubes are formed at a lower temperature than single-walled carbon nanotubes. Temperatures for MWNT growth are usually  $550^{\circ}\text{C}$  -  $750^{\circ}\text{C}$  and SWNT  $850^{\circ}\text{C}$  -  $1000^{\circ}\text{C}$ . Acetylene, ethylene, ethanol or methane is usually the hydrocarbon gas used and the most commonly catalysts are



nickel, cobalt, iron or a combination [5] [6] [18]. The typical yield for the CVD process is 20 to 100% [12].

Alan M. Cassell *et al.* synthesized gram quantities of single-walled carbon nanotube materials in 0.5h, which they grew on a novel silica-alumina multicomponent material covered with a Fe/Mo catalyst, using CVD with methane. The nanotube material they acquired consisted of bundled and individual SWNTs that were free of defects and amorphous carbon coating. The catalyst were calcined in air at 500°C then cooled to room temperature in air before the CVD process. The sample was heated from room temperature to 900°C in a Ar atmosphere, Ar gas was then replaced by  $CH_4$  (at a flowrate of 6000cm<sup>3</sup>/min). After the desired reaction time (2-45) min they switched to Ar and let the furnace cool to room temperature [19].

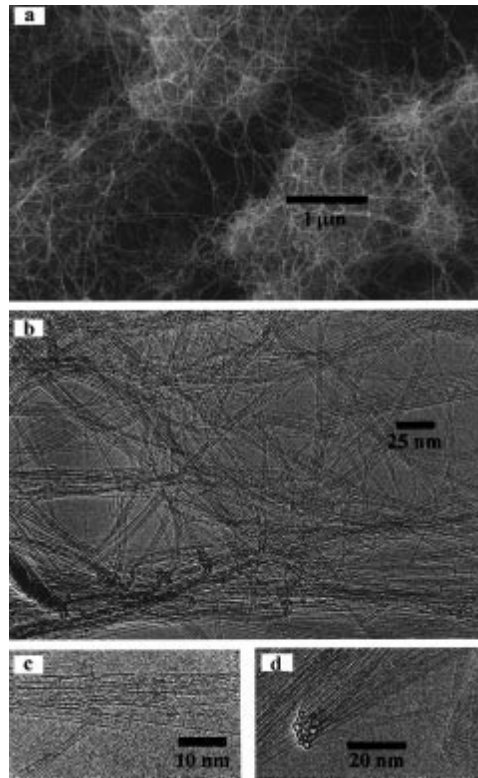


Figure 14: (a) SEM and (b-d) TEM images of SWNTs using the Fe/Mo/hybrid catalyst [19].

Ming Su *et al.* reported an improved CVD method for preparation of SWNTs with high productivity using a novel aerogel supported Fe/Mo catalyst that produced an amount of high quality SWNTs that was greater than 200% of the catalyst weight. The catalyst they used was prepared using a sol-gel technique and was followed by supercritical drying. The amount of

Mo and Fe was chosen so the molar ratio was  $\text{Mo:Fe:Al} = 0.16:1:16$ . In a typical experiment they put 50mg catalyst in an alumina boat and warmed it up to the reaction temperature ( $850^{\circ}\text{C} - 1000^{\circ}\text{C}$ ) under an Ar flow. They then switched to  $\text{H}_2$  flow for 30 minutes before switching to a flow of methane for a desired reaction time before it was turned off and Ar flow was turned back on and the temperature reduced to room temperature. The samples were characterized using TEM and SEM. For a typical 60min growth experiment at  $900^{\circ}\text{C}$  they got about 200% weight gain, the most weight gain they got were about 600% for 6.5h growth. Fig.15 shows one of their experiments where the weight gain was determined by thermogravimetric analysis (TGA) to be 100.2% [20].

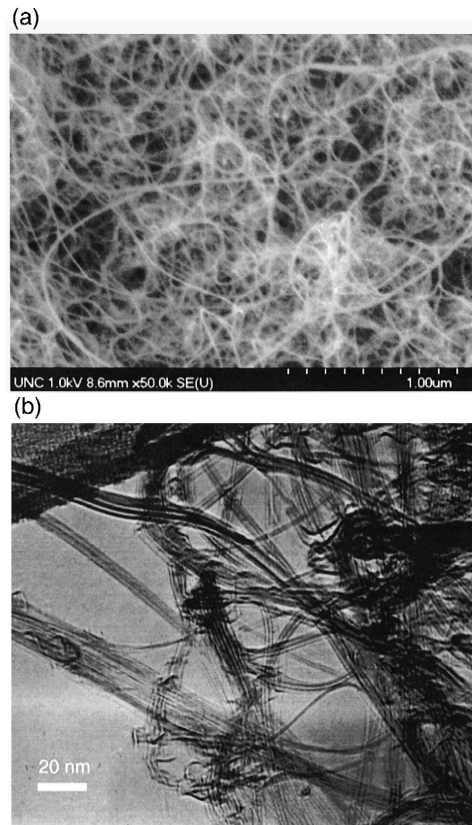


Figure 15: (a) SEM and (b) TEM image of SWNT sample that was prepared at  $900^{\circ}\text{C}$  with 1158 sccm  $\text{CH}_4$  flow, with Fe/Mo catalyst and 30 min reaction time [20].

Dalkeun Park *et al.* synthesized carbon nanotubes directly on stainless steel plates from acetylene and hydrogen gas mixture by sequential combination of rf plasma-enhanced chemical vapor deposition (PECVD) and thermal CVD. The PECVD was used for nucleation and initial growth while the CVD was used for further growth of the carbon nanotubes. The substrate used to grow the carbon nanotubes on were Stainless Steel 304. They pol-

ished the stainless steel plates with sandpaper, cleaned them in an ultrasonic bath with acetone and methanol sequentially, and afterward dipped in HF solution for a few minutes to etch the surface. The plates were put on the heater plate in the PECVD and was heated to the desired temperature, typically between 600°C to 850°C. The pressure in the reaction chamber 1 - 10 Torr with acetylene flow rate 7-30 sccm and hydrogen flow rate 20 - 90sccm and rf plasma power 60 - 100 W. After the PECVD procedure they turned off the RF power and stopped the flow of acetylene, introduced ammonia gas while they turned off the hydrogen. They raised the reactor pressure to atmospheric and adjusted the temperature of the heating block to the thermal CVD value, 600°C - 750°C. After they had reached the desired temperature acetylene flow was introduced again to resume carbon nanotube growth at 3 - 20 sccm together with an ammonia flow at 15 - 50 sccm. The samples were examined with SEM and Raman spectroscopy. Fig.16 shows SEM image of carbon nanotubes growth by PECVD for 1 min followed by thermal CVD for (a) 30 minutes and (b) 60 minutes. To the right on Fig.16 is a schematic diagram of the process[21].

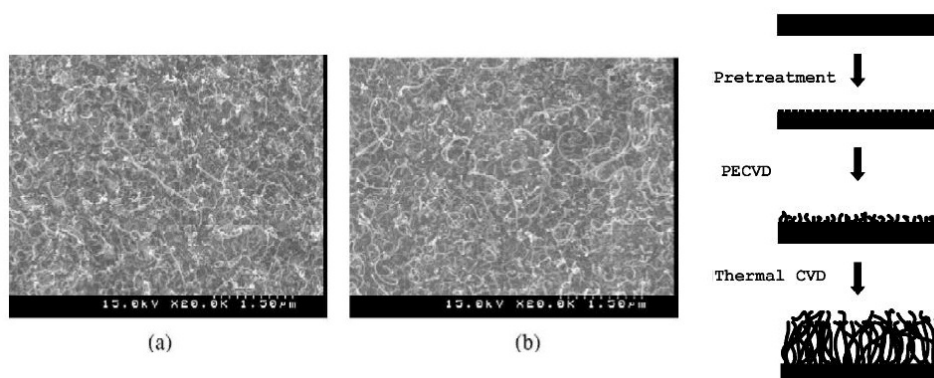


Figure 16: SEM images of the carbon nanotubes growth after 1 min with PECVD followed by (a) 30 minutes with thermal CVD (b) 60 minutes with thermal CVD. To the right is a schematic illustration showing the carbon nanotube synthesis [21].

Prahalad M. Parthangal *et al.* presented a method of growing aligned CNT arrays on a variety of metals, metal alloys and conductive ceramics by using a bimetallic iron/alumina composite catalyst. The substrates they used for growth of CNTs in their work were commonly used metals: highly doped Si, Au, Ag, Al, tungsten (W), platinum (Pt) and metal alloys: titanium nitride (TiN), nichrome (Ni-Cr) and steel. They sputtered or evaporated metal films (100 nm thick) onto silicon dioxide wafers, except for tungsten (W) where they used TEM grids and steel which were a hot-rolled steel plate. The substrates were loaded into an alumina boat and placed into a CVD furnace. They heated the the furnace to 625°C under a flow of Ar (200 sccm) and  $H_2$  (45 sccm) where they were typically annealed for 10

Substrate	CNT characteristics
Si	Uniform, well aligned
Au	Uniform, well aligned
Ag	Uniform, well aligned
Cu	Non-uniform, random growth
Al	Uniform, well aligned
Pt	No CNT growth
W	Uniform, well aligned
TiN	Uniform, well aligned
NiCr	Uniform, well aligned
Steel	Uniform, aligned, not well adhered

Table 1: Growth characteristics for CNT on various metals and metal alloys [22].

minutes. They then introduced acetylene ( $C_2H_2$ ). They grew the CNTs for 5 minutes before they stopped the acetylene gas and cooled the substrates to room temperature in Ar.

In all the metal substrates, except Pt, there was nucleation and growth of carbon nanotubes. In Table 1 is the results of the CNT growth on the various substrates. The diameter of the CNTs for Si, Au, Ag, Cu, Al and W were approximately 10 to 20 nm, and a few tens of micron in length. The overall CNT arrays structure were well aligned vertically to the substrate surface. Fig.17 shows SEM images of the metal substrates with their CNT arrays. They also managed to grow well aligned carbon nanotube arrays on metal alloys and conductive ceramics such as TiN, NiCr and steel where the catalyst was dispersed. Fig.18 shows SEM images of the metal alloys and conductive ceramics. It was also observed that the carbon nanotube arrays that were grown on steel were very weakly adhered and peeled off from the surface readily [22].

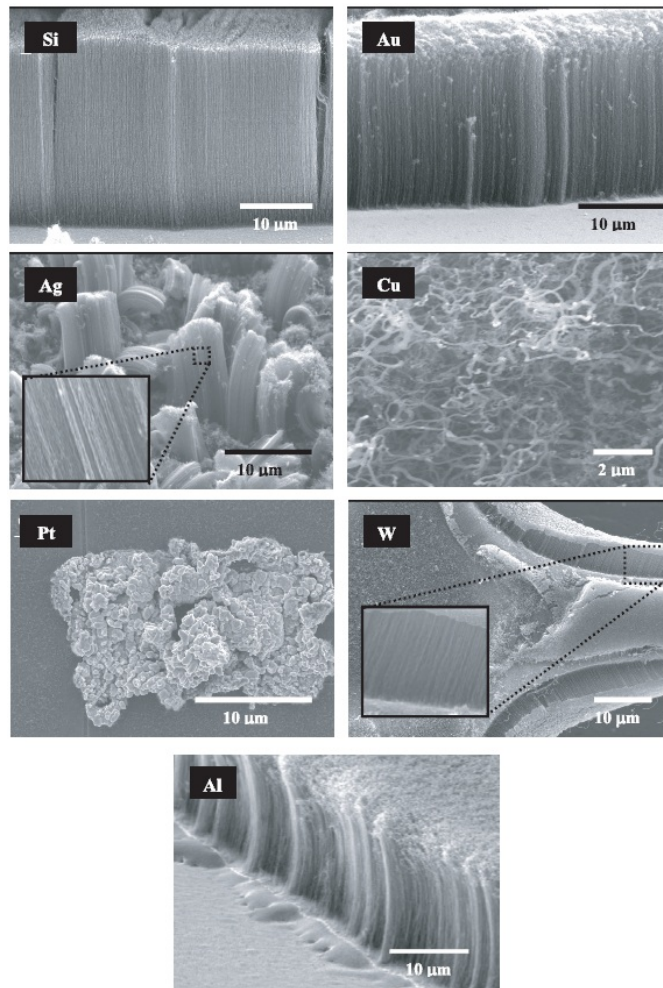


Figure 17: SEM images of the metal substrates. All of the substrates supported CNT growth with the exception of Pt. The CNTs for all the metals were well aligned vertically to the sample surface except Cu which were thicker and randomly oriented [22].

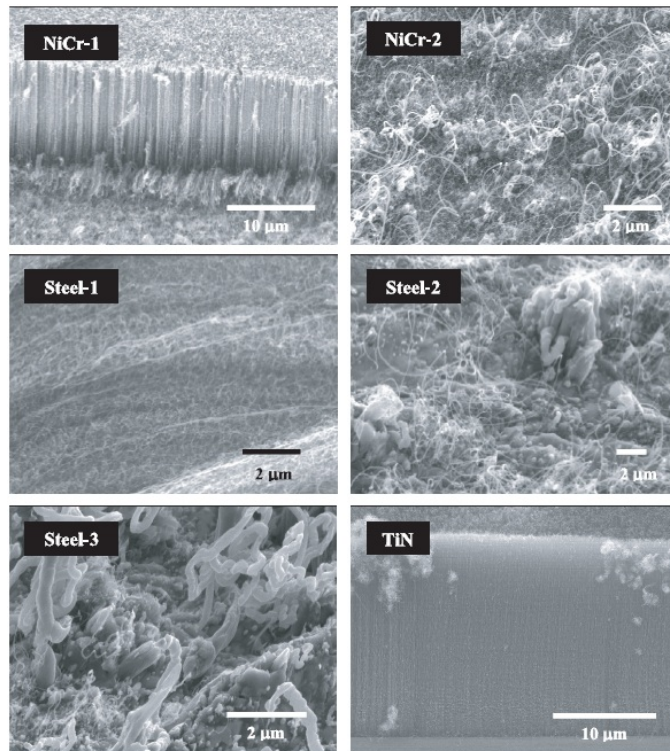


Figure 18: SEM images of the metal alloys nichrome (NiCr) and steel and a conductive ceramic (TiN). Carbon nanotubes grew vertically where the catalyst was applied (NiCr-1, Steel-1, TiN). CNTs, fiber and amorphous deposits were observed to grow where the catalyst was not applied (NiCr-2, Steel-2, Steel-3). This is because the intrinsic presence of catalyst materials in these substrates (Ni, Fe) [22].

### 2.3.4 PECVD

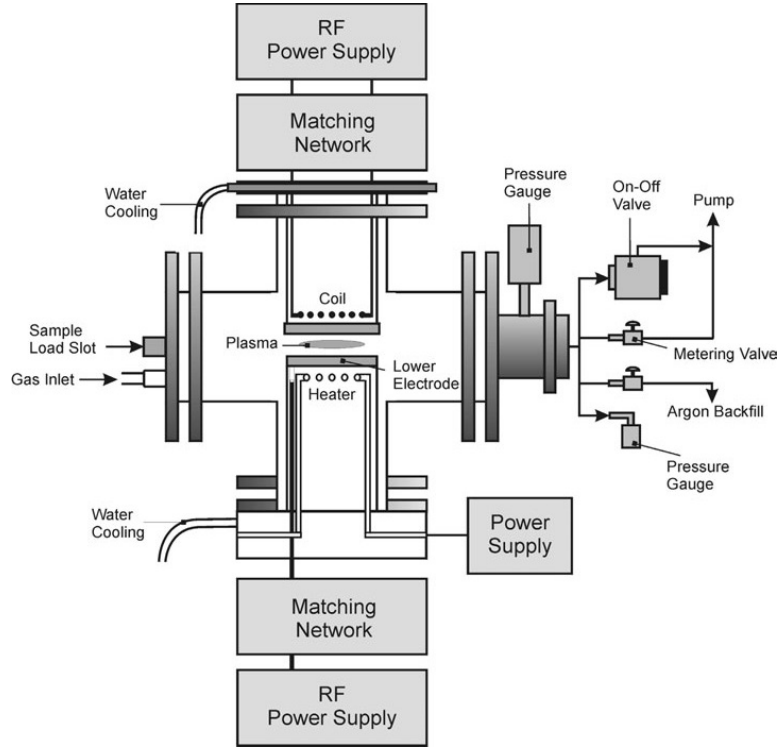


Figure 19: A schematic of a PECVD-setup [23].

The plasma enhanced chemical vapor deposition process is similar to the CVD process. The plasma is created by a strong electrical field during the growth process and this causes the growth of the carbon nanotubes to follow the direction of the electrical field [24]. By using plasma it is possible to create vertically aligned carbon nanotubes on a surface.

Satoshi Sugimoto *et al.* developed a method for growing carbon nanotubes directly on the surfaces of stainless 304. They used plasma-assisted chemical vapor deposition and formed CNTs at comparatively low temperature, thus avoiding annealing and degradation of the stainless steel. Stainless steel contains the catalytic materials needed for carbon nanotube formation and thus coating the stainless steel with a catalyst is not needed. Their most successful result was when they pre-heated the stainless steel at  $300^{\circ}\text{C}$  for 20 minutes before they started the PECVD process. When the temperature reached  $550^{\circ}\text{C}$  in vacuum they introduced hydrogen gas at 50 sccm into the chamber and used plasma discharge to clean the substrate surface at a pressure of 1000 Pa for 20 minutes. When this was done they introduced methane gas instead of hydrogen at 50 sccm and the plasma discharge was maintained for 60 more minutes.

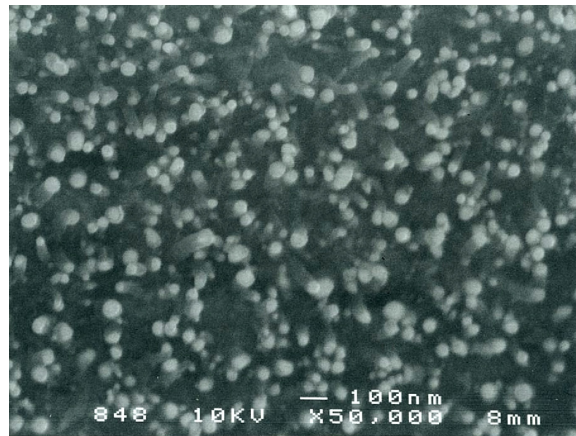


Figure 20: SEM image of the stainless steel surface after the pretreatment and PECVD process [25].

Their decision to pretreat the surface came after their first attempt that was without preheating for 20 minutes at 300°C where carbon nanotubes grew only in some areas of the surface. They used a TEM-EDX to analyse the particles in the CNT tips, which was almost exclusively Fe. The stainless steel surface is covered with a thin layer of chromium-oxide so they used the pretreatment to supply more Fe to the component on the surface. With this they showed that MWNTs can be grown uniformly on the surface of stainless steel as seen in Fig.20 [25].

Y. H. Man *et al.* synthesized carbon nanotubes from Ar-CH<sub>4</sub> mixtures using rf-plasma enhanced chemical vapor deposition at 500°C. H<sub>2</sub> and NH<sub>3</sub> reduction gases were found unnecessary. They investigated the relationship between growth conditions of carbon nanotubes and the plasma condition. The growth was strongly influenced by the plasma condition. Their carbon nanotube growth experiments consisted of three steps: (1) heat treatment, (2) Ar plasma pretreatment and (3) Ar-CH<sub>4</sub> plasma treatment. As a substrate they deposited a 17nm thick Al bufferlayer between a Fe catalyst layer (3 nm) and a Si wafer by electron-beam evaporation at room temperature. They evacuated the PECVD reaction chamber to the base pressure (10<sup>-5</sup>) Pa and heated the substrate. They then introduced Ar gas and maintained it at 0.9 Torr with a flowrate of 100 sccm when the synthesis temperature reached 500°C. Ar plasma was then introduced at 30W for 5 minutes as a pretreatment for the catalyst. CH<sub>4</sub> gas was then introduced and kept at 1 Torr. After 20 min synthesis the sample was cooled down. They also tested various rf power (30, 50, 70, 100 and 150W) and different CH<sub>4</sub> / Ar ratios (1:0, 1:2, 1:5) for parametric study. Fig.21 shows SEM images of the carbon nanotubes growth under different rf power [26].



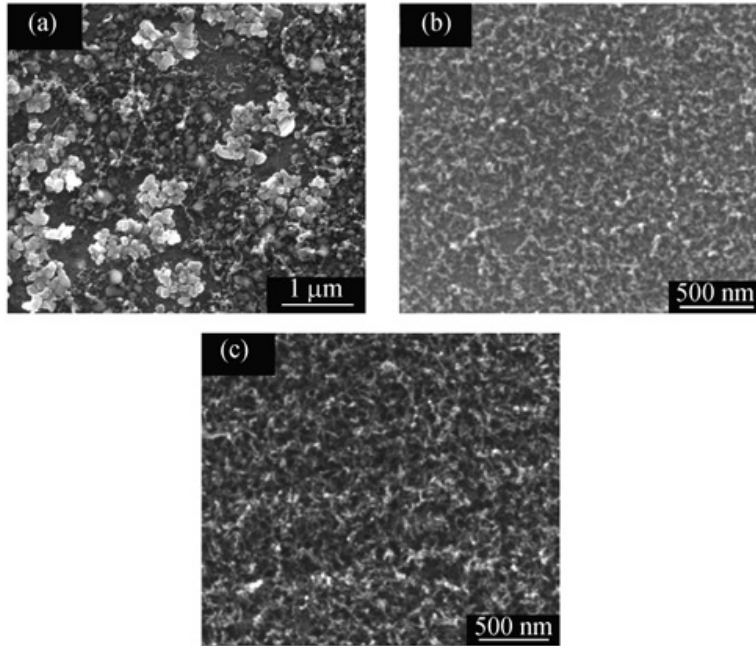


Figure 21: SEM images of carbon nanotubes growth at different rf power. (a) 30 W, (b) 70 W, (c) 100 W [26].

## 2.4 Surface structuring

Carbon Nanotube have been used for surface structuring, to change the surface's properties. As an example Kenneth K.S. Lau *et al.* used the nanoscale roughness of vertically aligned carbon nanotubes which they covered with a thin hydrophobic poly(tetrafluoroethylene)(PTFE) coating to create a superhydrophobic surface down to a microscopic level. The vertically aligned carbon nanotube forest was created with PECVD. They sintered a thin nickel (Ni) film (5 nm) on a oxidized silicon substrate at 650°C which created nickel catalyst islands. Carbon nanotubes grew from these island in a DC plasma discharge of acetylene (75 sccm) and ammonia (200 sccm) at a partial pressure of 4 Torr. Fig.22(c) shows a waterdroplet suspended on the PTFE-coated carbon nanotube forest. The contact angles measurements were performed by using the sessile drop method. The advancing and receding contact angles of the treated forest are 170° and 160° [27].

Fig.23 shows the results for a coated carbon nanotube forest with nanotube diameter 50nm and heights ranging from 0.2 to 1.1  $\mu\text{m}$ .

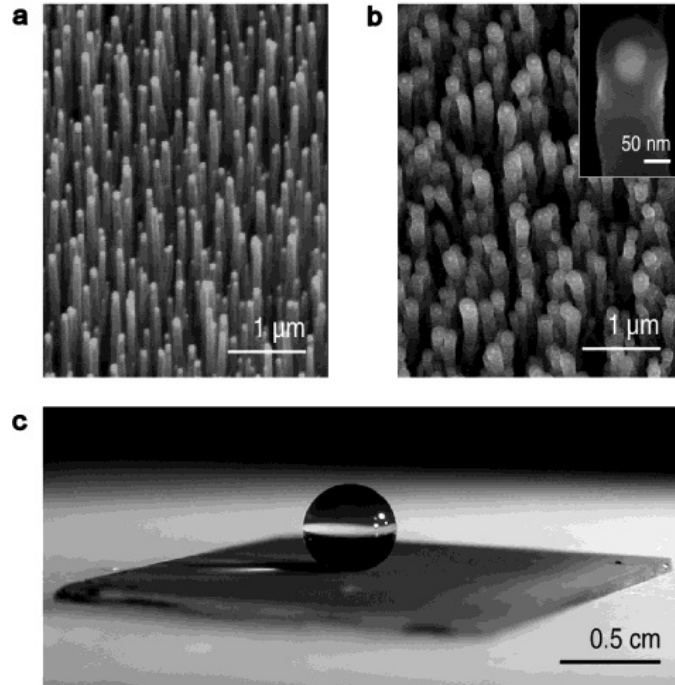


Figure 22: (a) Shows SEM image of the grown CNT forest by PECVD with nanotube diameter of 50nm and a height of 2  $\mu\text{m}$ . (b) The PTFE-coated forest after tge HFCVD treatment. (c) an essentially spherical water droplet suspended on the forest coated with PTFE [27].

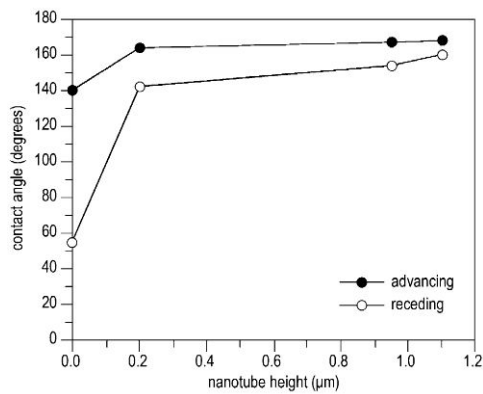


Figure 23: Graph of dynamic water contact angle measurements on carbon nanotube forest. The hysteresis, difference between advancing and receding angles, decreases with increasing forest height for the same diameter and spacing [27].

### 3 Experiments

The intenson with these experiments were to see if we could grow carbon nanotubes directly on the surface of stainless steel. The sample materials that were used were Stainless Steel 316L and Arctic Steel 420MPa. All the samples were about  $10\times 10$  mm and 2mm thick or less. The SS316 samples were cut from a 3mm thick plate(Fig.24(a)) and then sanded down to 2mm, so they were under the height requirements for the FIB. All the samples were cleaned in acetone in a utrasonic bath and then washed with ethanol, then isopropyl alcohol and deionized water before the PECVD. The samples were put onto a Si wafer in the loadlock chamber wich then was pumped down to  $6\times 10^{-5}$  Torr before the samples were loaded into the chamber. Each process was started with pump-purge cycle before the chamber was pumped to base pressure. After this either the conditioning or pre-treatment was started followed by the deposition process. After this it was a  $3\times$  pump-purge cycle before pump to base pressure and the whole PECVD process was finished. The wafer with the samples was then retracted out to the loadlock chamber which was then ventilated and the samples taken out.

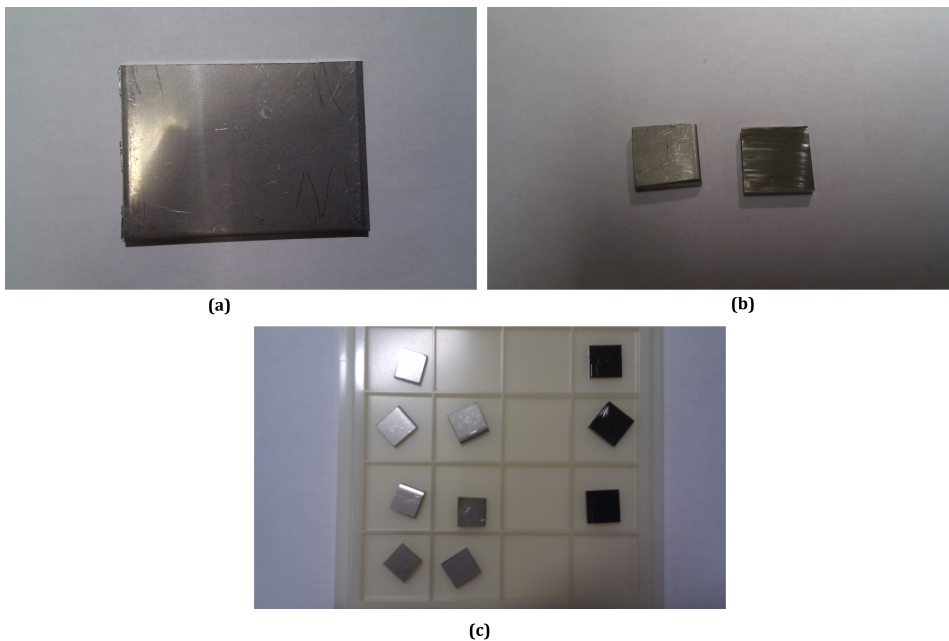


Figure 24: Image of plate where stainless steel samples were cut from (a). Image of untreated samples (b). Image of one of the samples holder boxes (c).

### 3.1 Instruments

#### 3.1.1 Plasma Enhanced Chemical Vapor Deposition

The PECVD machine used was a “PlasmaLab system 100 - PECVD” from Oxford Instruments with the available process gases:  $\text{SiH}_4$  50sccm,  $\text{NH}_3$  50sccm,  $\text{N}_2\text{O}$  1000sccm,  $\text{N}_2$  2000sccm, Ar 2000sccm,  $\text{CF}_4$  500sccm and  $\text{CH}_4$  100sccm, 10% $\text{PH}_3$ /Ar 50sccm, 0,1% $\text{B}_2\text{H}_6$ /0,23% $\text{H}_2$ /Ar 50sccm. The RF 0-300W, frequency up to 13.56 MHz and a pressure from 10mTorr - 2Torr. Fig.25 shows the PECVD machine at NTNU NanoLab

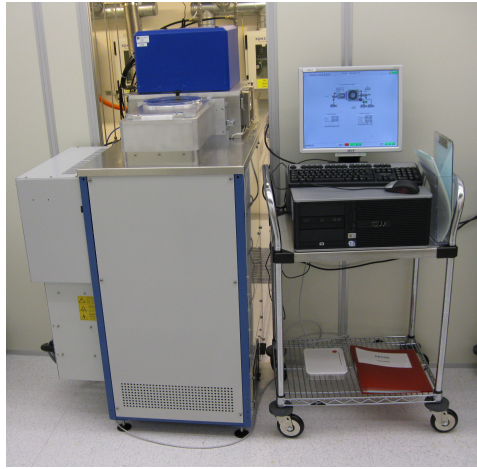


Figure 25: PECVD machine at NTNU NanoLab [28].



Figure 26: FIB machine with SEM at NTNU Nanolab [29].

### 3.1.2 Focused ion beam/Scanning electron microscope

To observe the carbon nanotubes the SEM in the FIB was used. The samples were cut in  $10 \times 10$  mm and was under 2 mm to fit the height requirements of the FIB. Fig.26 shows the FIB machine at NTNU NanoLab.

## 3.2 Recipes

The recipes were inspired by two articles, Satoshi Sugimoto *et al.* “Carbon nanotube formation directly on the surface of stainless steel materials by plasma-assisted chemical vapor deposition” [25] and Y. H. Man *et al.* “Influence of plasma condition on carbon nanotube growth by rf-PECVD” [26]. The recipes was limited to 500°C in the start since this was new recipes which wasn’t tried at NTNU NanoLab before. The use of catalyst, pre-heating and conditioning of the samples can be seen in Table.2 while the pretreatments and deposition recipes can be seen in Table.3 and Table.4. The cobolt and gold catalysts on some of the samples were curious experiments to see if they had any effect at all, that is why they were placed together in the PECVD with another sample without the catalyst. The 5nm layer of catalyst were deposited with electron beam evaporation.

Samples SS316L-08 to SS316L-11 are only pretreated. The pretreatment conditions was: 40 sccm NH<sub>3</sub>, 100 sccm N<sub>2</sub>, 200 mTorr with strike pressure at 1000 mTorr, 20W RF and for 10 minutes at 500°C, 550°C, 600°C and 650°C. This was a request from Oxford Instruments, which we had asked for guidance, so they could see the different surfaces at different temperatures. In Fig.32 we can see the difference on the grain surface depending on the temperature.

Sample	Substrate	Catalyst	Preheating	Conditioning
SS316L-01	SS316L	-	20 min @ 300°C	-
SS316L-02	SS316L	-	-	-
SS316L-03	SS316L	Au (5nm)	-	-
SS316L-04	SS316L	-	-	10 min 500°C Ar 100 sccm 900 mTorr
SS316L-05	SS316L	Cobolt	-	10 min 500°C Ar 100 sccm 900 mTorr
SS316L-06	SS316L	-	-	-
SS316L-07	SS316L	Cobolt	-	-
SS316L-12	SS316L	-	-	-
AS420-01	AS420	-	-	-
SS316L-13	SS316L	-	-	10 min 500°C Ar 100 sccm 900 mTorr
AS420-02	AS420	-	-	10 min 500°C Ar 100 sccm 900 mTorr
SS316L-14	SS316L	-	20 min @ 300°C	-
AS420-03	AS420	-	20 min @ 300°C	-

Table 2: Table showing substrate, catalyst, preheating and conditioning of the samples

Sample	Pretreatment	Process	Results
SS316L-01	NH <sub>3</sub> 40 sccm N <sub>2</sub> 100 sccm 200 mTorr RF 20W 1 min Plasma didn't start	Ar 285 sccm CH <sub>4</sub> 50 sccm 50kHz, 20W LF 500°C 1900 mTorr 60 min	No growth
SS316L-02 SS316L-03	NH <sub>3</sub> 40 sccm N <sub>2</sub> 100 sccm 200 mTorr Pressure Strike @ 1000 mTorr rate 10 20W RF 500°C 10 min	NH <sub>3</sub> 50 sccm CH <sub>4</sub> 10 sccm 20W RF 500°C 1000 mTorr 60 min	No growth
SS316L-04 SS316L-05	Ar 100 sccm 900 mTorr 30W RF 500°C 5 min	Ar 200 sccm CH <sub>4</sub> 100 sccm 100W RF 500°C 1000 mTorr 30 min	No growth
SS316L-06 SS316L-07	NH <sub>3</sub> 40 sccm N <sub>2</sub> 100 sccm 200 mTorr Pressure Strike @ 1000 mTorr rate 10 20W RF 500°C 10 min	NH <sub>3</sub> 50 sccm CH <sub>4</sub> 10 sccm 150W RF 500°C 1000 mTorr 60 min	No growth

Table 3: Table showing pretreatment, process, results.



Sample	Pretreatment	Process	Results
SS316L-12 AS420-01	NH <sub>3</sub> 40 sccm N <sub>2</sub> 100 sccm 200 mTorr Pressure Strike @ 1000 mTorr rate 10 20W RF 500°C 10 min	NH <sub>3</sub> 50 sccm CH <sub>4</sub> 10 sccm 150W RF 550°C 1000 mTorr 60 min	No growth
SS316L-13 AS420-02	Ar 100 sccm 900 mTorr 30W RF 550°C 5 min	Ar 200 sccm CH <sub>4</sub> 100 sccm 100W RF 1000 mTorr 550°C 30 min	No growth
SS316L-14 AS420-03	NH <sub>3</sub> 40 sccm N <sub>2</sub> 100 sccm 200 mTorr Pressure Strike @ 1000 mTorr rate 10 20W RF 550°C 10 min	Ar 285 sccm CH <sub>4</sub> 50 sccm 20W RF 1900 mTorr 550°C 60 min	No growth

Table 4: Table showing pretreatment, process and results.

### 3.3 Results

Unfortunately we were not able to observe carbon nanotube growth on any of the samples with the PECVD process. One of the most interesting samples were SS316L-05, which had a 5 nm cobolt catalyst, Fig.29 shows one of the interesting areas of this sample. It is difficult to say if it's carbon deposits or something that has happened to the cobolt catalyst. These areas was randomly scattered around the sample. The other sample which stood out was SS316L-07, Fig.31, which also had a 5nm cobolt catalyst. It was difficult to get good pictures of these areas in the SEM, it is unknown if it's carbon or if it's cobolt.

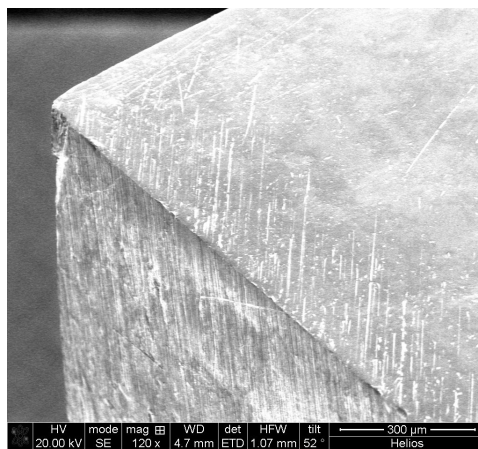


Figure 27: SEM picture of sample SS316L-02 which were the only polished sample.

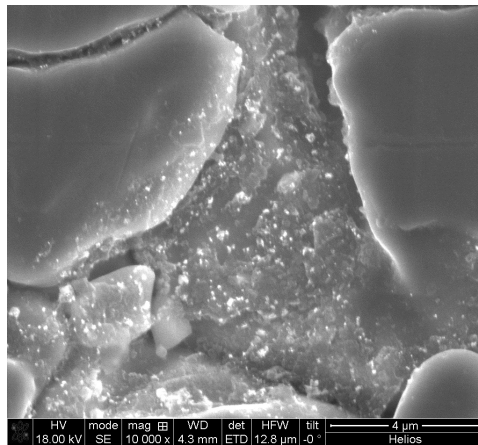


Figure 28: SEM picture of sample SS316-04 showing the area between grains.

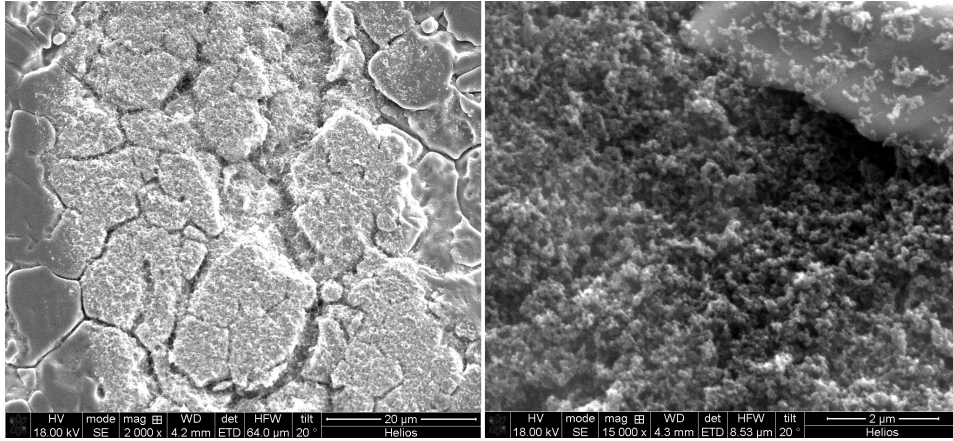


Figure 29: SEM image of SS316L-05 showing area of interest, unknown if carbon or cobalt. There was several of these areas randomly on the sample

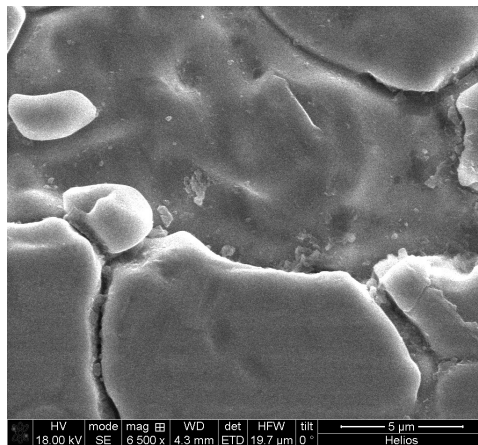


Figure 30: SEM image of SS316L-06. No traces of carbon deposition on the sample.

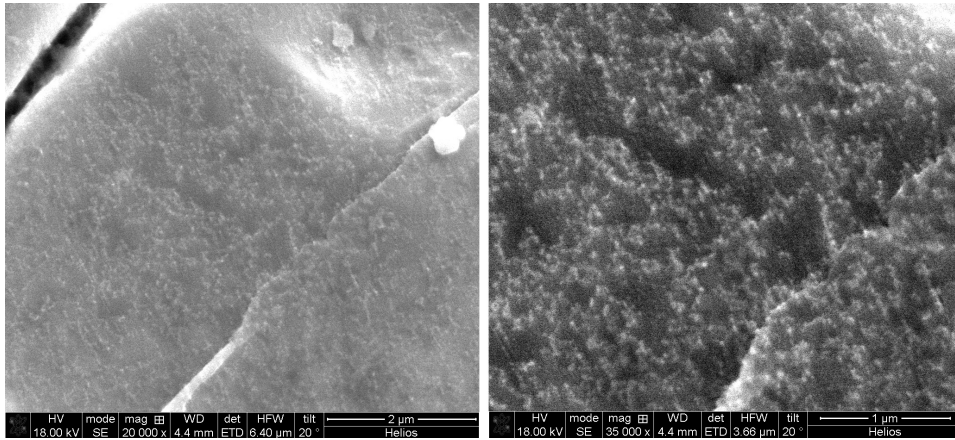


Figure 31: SEM image of SS316L-07 showing a interesting area. Unknown if it is carbon nanotubes or cobolt. There was several of these areas randomly on the sample.

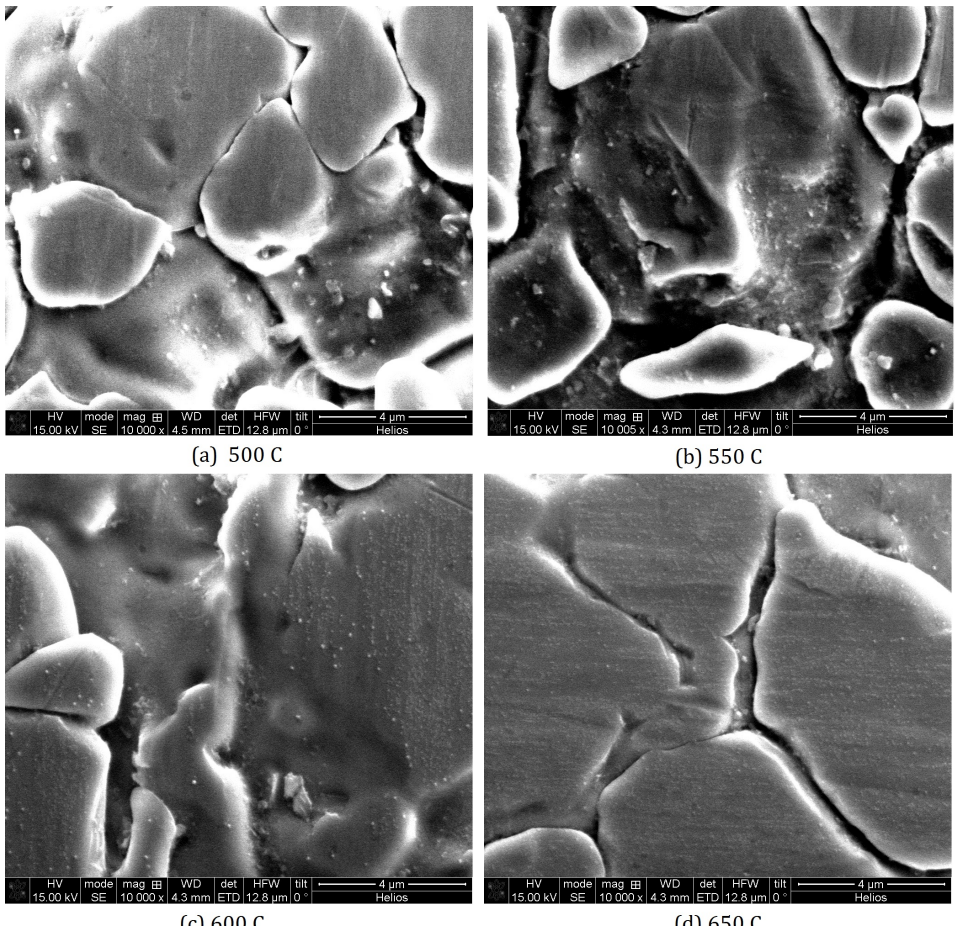


Figure 32: SEM images showing the pre-treatment effect on different temperatures. (a) 500°C, (b) 550°C, (c) 600°C and (d) 650°C.

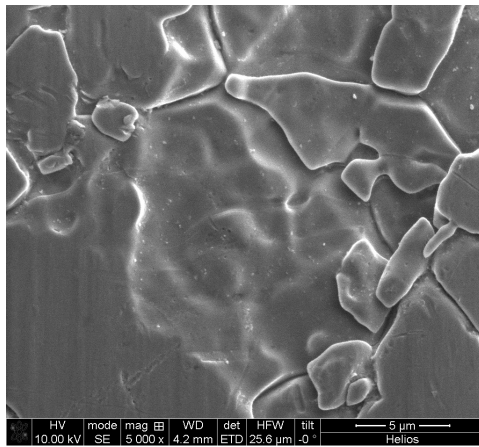


Figure 33: SEM image of SS316L-12. No traces of carbon deposition on the sample.

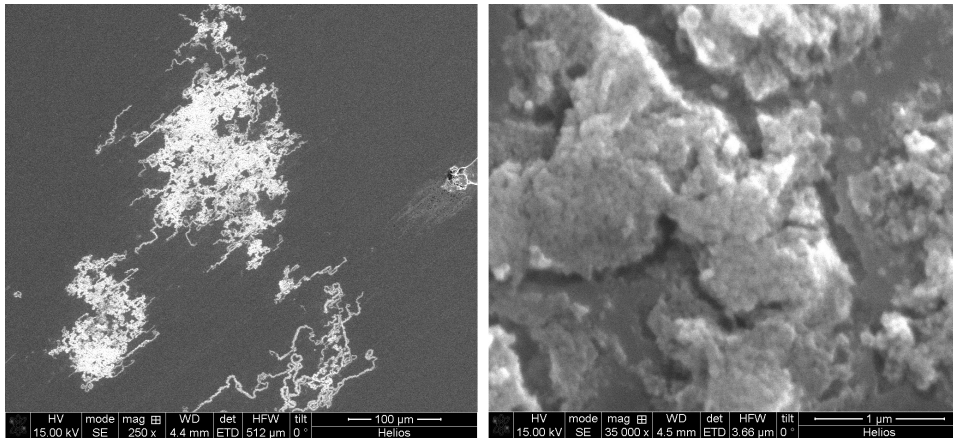


Figure 34: SEM images of AS420-01 and what i belive to be rust on the surface. No traces of carbon deposition.

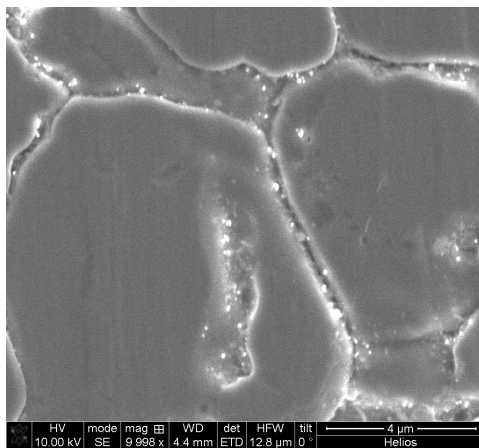


Figure 35: SEM image of SS316L-13. No traces of carbon deposition on the sample.

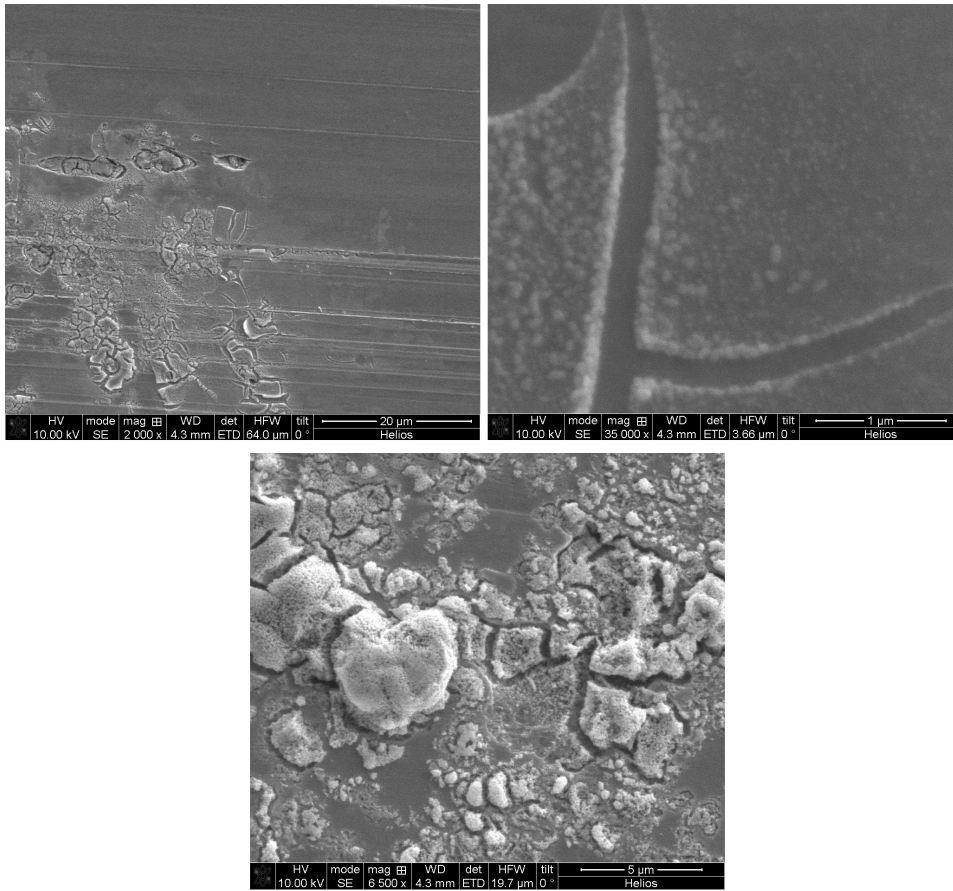


Figure 36: SEM images of AS420-02 and what i belive to be rust on the surface. No traces of carbon deposition.

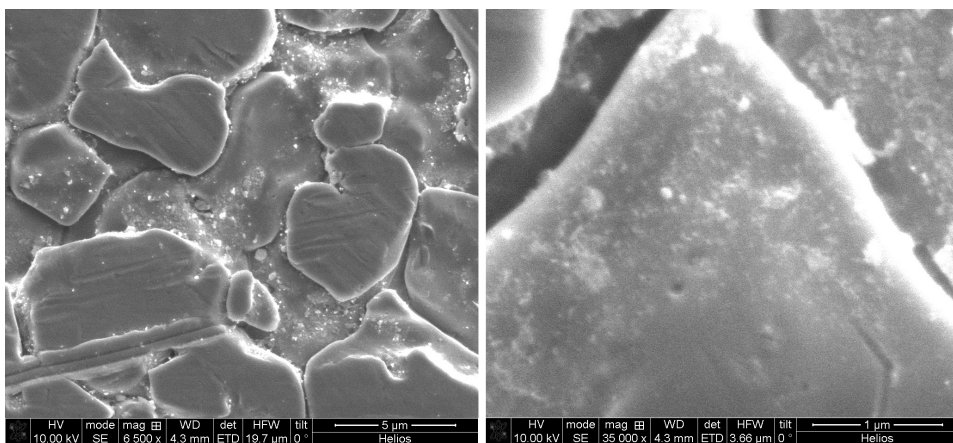


Figure 37: SEM image of SS316L-14. Showing some interesting areas on th edges of grains but no visible CNT growth.

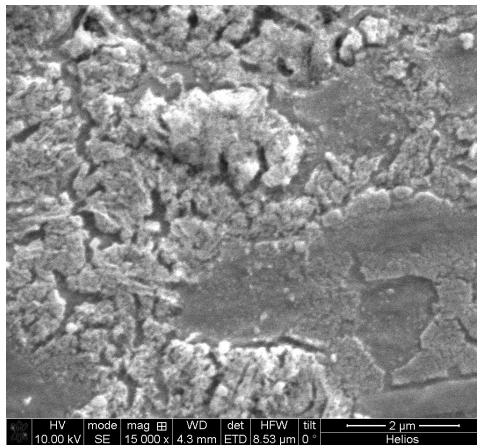


Figure 38: SEM image of AS420-03 and what i belie to be rust on the surface. No traces of carbon deposition

## 4 Conclusion

The most cost effective way to produce carbon nanotubes are either with CVD or PECVD process. The advantage with PECVD is that you get aligned carbon nanotubes in the direction of the electric field. This is an advantage for surface structuring with carbon nanotubes if you want to use the roughness that a carbon nanotube forest can give you.

The experiments trying to grow carbon nanotubes directly on Stainless Steel 316L and Arctic Steel 420MPa conducted at the NTNU NanoLab proved harder and more time consuming than anticipated. I had hoped for some feedback from Oxford Instruments, regarding images of the pretreated surfaces that they asked for, in which direction we could have taken steps closer to acquire the goal of growing carbon nanotubes in the PECVD here at NTNU. With higher temperatures and more time to test different variations of the recipes we started on I think we would have seen CNT growth on our samples. I don't think we were far from our goal.

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