NTNU – Trondheim
Norwegian University of
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Innovative Utilization of Carbon Nanotubes in Marine and Offshore Oil/Gas Applications

Øyvind Våland

Master of Science in Mechanical Engineering
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Supervisor: Christian Thaulow, IPM

Norwegian University of Science and Technology
Department of Engineering Design and Materials

THE NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

MASTER'S THESIS SPRING 2013
FOR
STUD.TECHN. ØYVIND VÅLAND

INNOVATIVE UTILIZATION OF CARBON NANOTUBES IN MARINE AND OFFSHORE OIL/GAS APPLICATIONS

Innovativ utnyttelse av karbonnanorør i marine og offshore olje/gass anvendelser

Carbon nanotubes (CNTs) is an emerging material proven to hold exceptional properties. The mechanical strength and its electrical and thermal conductivity surpass all known materials. Now, 20 years after its discovery, the material is about to make its entry into the commercial market. The project thesis of the candidate went on reviewing these twenty years including CNT synthesis, properties, characterization and applications. The project found that researchers are reaching consensus of the material behavior and that the manufacturers of CNTs may be about to start a price war. It's the perfect time to develop and patent products making use of CNTs brilliant properties.

This master thesis shall explore the use of CNTs in commercial applications. The goal is to initiate the development of products with CNTs as an essential constituent, either by replacing a current material or in the development of brand new applications. Especially applications of Norwegian interests shall be in focus, such as marine and oil/gas.

If time allows, CNT can be manufactured and tested at NTNU Nanolab and at the Nanomechanical lab at IPM. The student is also encouraged to contact industry for dialogues and creative discussions.

The following tasks shall be carried out:

- Locate applications where the use of carbon nanotubes may be advantageous.
- Make contact with industry and seek interest in the project
- Initiate product development of at least two applications.
- Test the CNT eligibility for at least one of the products.

The thesis should include the signed problem text, and be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Masteroppgave" (http://www.ntnu.no/ipm/masteroppgave). This sheet should be updated one week before the Master's thesis is submitted.

The thesis shall be submitted electronically via DAIM, NTNU's system for Digital Archiving and Submission of Master's thesis.

Contact persons:

Prof. Torgeir Welo
Head of Division

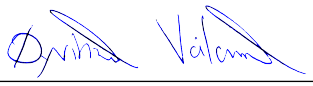
Prof. Christian Thaulow
Supervisor

NTNU
Norges teknisk-
naturvitenskapelige universitet
Institutt for produktutvikling
og materialer

Declaration of Authorship

I, Øyvind Våland, declare that this thesis titled, 'Innovative Utilization of Carbon Nanotubes in Marine and Offshore Oil/Gas Applications' and the work presented in it are my own. I confirm that:

- This work was done wholly while in candidature for a master's degree at NTNU.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Sign: 

Place / Date: Trondheim / 10th June 2013

"Twenty years from now you will be more disappointed by the things that you didn't do than by the ones you did do. So throw off the bowlines. Sail away from the safe harbor. Catch the trade winds in your sails. Explore. Dream. Discover."

H. Jackson Brown Jr.

Photo: Mørenot AS

Abstract

Innovative Utilization of Carbon Nanotubes in Marine and Offshore Oil/Gas Applications

by Øyvind Våland

Norwegian University of Science and Technology
Department of Engineering Design and Materials

Nations with an established prominence in nanotechnology will lead the development of the future society by offering superior products to the global market. This thesis encourages Norwegian maritime industries to recognize the potential in carbon nanotubes (CNTs) and mark their position as leading innovators. Push innovation has been used to bring science from research papers into business concepts including product design and cost analysis. Material challenges have been discussed with partners in aquaculture, shipping and offshore oil/gas in order to find viable use of CNTs. Two concepts, net cage of CNT yarn in fish farming and oil drier with CNT membrane for hydraulic and lubricating systems, have been developed. The net cage is a potential health risk, but the superhydrophobic and superoleophilic properties of CNT membranes provide a novel and promising way of separating water and oil. Fabrication of prototype in NTNU Nanolab have been attempted by growing vertically aligned CNTs by plasma-enhanced chemical vapor deposition, but not completed.

Sammendrag

Innovativ utnyttelse av karbonnanorør i marine og offshore olje/gass anvendelser

av Øyvind Våland

Norges Teknisk- Naturvitenskapelige Universitet
Institutt for Produktutvikling og Materialer

Nasjoner med spisskompetanse på nanoteknologi vil lede utviklingen av framtidens samfunn ved å tilby overlegne produkter til det globale markedet. Denne masteroppgaven oppmuntrer norsk maritim industri til å se potensialet i karbonnanorør (CNT) og markere sin posisjon som ledende innovatører. Push-innovasjon har blitt brukt til å bringe vitenskap fra forskningsartikler til forretningskonsepter med bidrag av produktdesign og kostnadsanalyse. Materialutfordringer har vært diskutert med bedrifter innen fiskeoppdrett, shipping og offshore olje og gass for å finne potensiell bruk av CNT. To konsepter, not av CNT tråd i fiskeoppdrett og oljetørker med CNT membran, er utviklet. CNT kan gi høy styrke til fiskenøter, men er også en helsemessig risiko. De superhydrofobiske og superoleophiliske egenskapene til en CNT membran vil være optimale for å separere olje og vann i hydraulikk- og smøresystemer. Konseptene er skissert opp og fabrikasjon av prototyper i NTNU Nanolab ble forsøkt. Vertikale CNT ble dyrket ved hjelp av plasmaassistert kjemisk damp deponering, men ingen prototype ble ferdigstilt.

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Preface

This is the master's thesis of Øyvind Våland (Oeyvind Vaaland), a work of 30 credits in the 10th semester at the Norwegian University of Science and Technology (NTNU). The work was done from the 14th of January 2013 to the 10th of June 2013 (20 weeks).

The context of this paper is set by the task description in the very first pages. Readers are expected to know intermediate level of science.

Quantities in this document are expressed according to *The International System of Units*, 8th edition (2006) published by The International Bureau of Weights and Measures. However, some non-SI units are too well established to be converted to SI and are listed in the section *Units*. All calendar dates are expressed in the sequence day-month-year. The thesis is written in English to reach a wider audience and because it is the established language in this field of science.

 Supporting material are available at DAIM (http://daim.idi.ntnu.no/) and at http://vaaland.priv.no.

The author would like to acknowledge the assistance received by:

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A special thanks to Prof. Liangbing Hu at The University of Maryland for introducing the author to the field of nanotechnology.

Abbreviations

ABC	**A**ctivity **B**ased **C**osting
CAD	**C**omputer-**A**ided **D**esign
CNT	**C**arbon **N**ano**T**ube
COO	**C**ost **o**f **O**wnership
CVD	**C**hemical **V**apor **D**eposition
DWCNT	**D**ouble-**W**alled **C**arbon **N**ano**T**ube
HACNT	**H**orizontally **A**ligned **C**arbon **N**ano**T**ube
HRTEM	**H**igh-**R**esolution **T**ransmission **E**lectron **M**icroscopy
MCC	**M**icroelectronics **C**omputer Technology **C**orporation
MEMS	**M**icro**E**lectro**M**echanical **S**ystems
MWCNT	**M**ulti-**W**alled **C**arbon **N**ano**T**ube
NorFab	**Nor**wegian infrastructure for micro and Nano**Fab**rication
PECVD	**P**lasma-**E**nhanced **C**hemical **V**apor **D**eposition
RTP	**R**apid **T**hermal **P**rocessing
SEM	**S**canning **E**lectron **M**icroscopy
SIA	**S**emiconductor **I**ndustry **A**ssociation
SWCNT	**S**ingle-**W**alled **C**arbon **N**ano**T**ube
TEM	**T**ransmission **E**lectron **M**icroscopy
VACNT	**V**ertically **A**ligned **C**arbon **N**ano**T**ube
WACVD	**W**ater-**A**ssisted **C**hemical **V**apor **D**eposition

Units

Micrometer	μm	=	10^{-6} m
Nanometer	nm	=	10^{-9} m
Picometer	pm	=	10^{-12} m
Gigapascal	GPa	=	10^{9} Pa
Megapascal	MPa	=	10^{6} Pa
Torr	Torr	=	133,3224 Pa
Millitorr	mTorr	=	13,33224 Pa
Standard Cubic Centimeters per Minute	sccm	=	1 cm^3/min
Tex	tex	=	1 g/km
Tenacity	N/tex	=	1 GPa/(g/cm^3)
Norwegian Krone	NOK	≈	5,80 USD

Chapter 1

Introduction

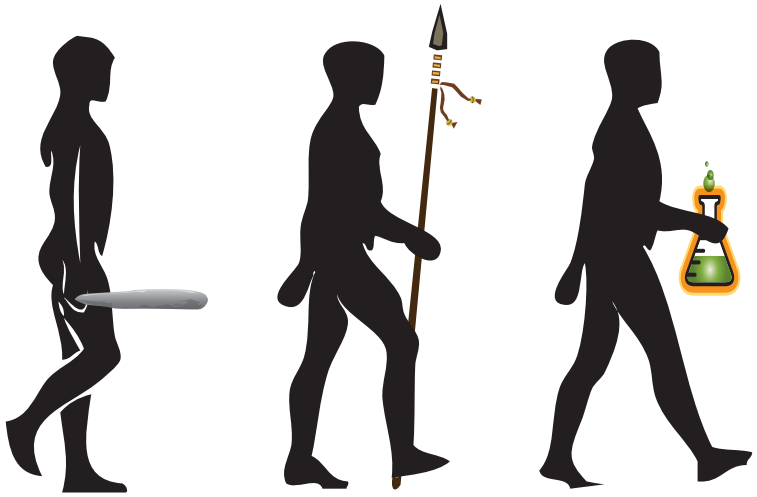


FIGURE 1.1: The evolution of material science from stone clubs to dispersed carbon nanotubes. Adapted illustration [1].

The discovery of materials may have a great social impact, making a big mark in history. The stone age gave us the skills of carving tools and the bronze age gave us the ability to cast metals. Now, the science of nanotechnology is making an entrance in what is referred to as the *nano age*. We are able to construct an endless variety of materials using a bottom up approach. This thesis is an exploration of our new capabilities in maritime environments by the use of carbon nanotubes.

1.1 Opportunity

The carbon nanotube (CNT) was discovered about twenty years ago by Sumio Iijima and was quickly made famous for its predictions of brilliant properties [2]. A CNT is a tube made of carbon atoms in a hexagonal pattern and with diameter in the range of 0,5 – 2 nm, hence a nanomaterial (Fig. 1.2). Scientifically, the material has been examined by thousands of researchers and the amounts of hits on Google Scholar have exceeded half a million articles. Commercially however, the material has yet to make its true entry. Some products exist, but there is still some hesitation and reluctance by both manufacturers and consumers partly due to high costs and possible health risks.

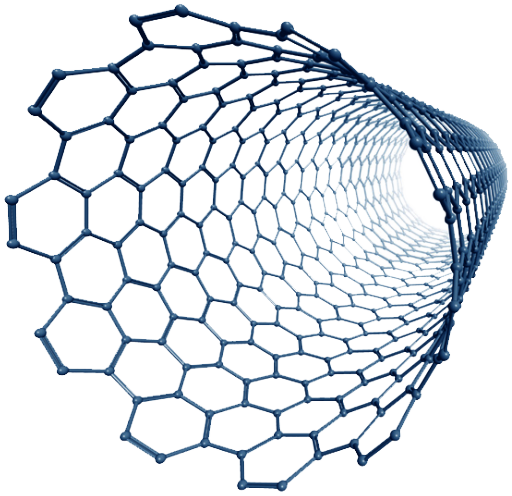


FIGURE 1.2: Illustration of a carbon nanotube. At each juncture there is a carbon atom, the lines in between illustrate atomic bonds [3].

Currently, USA, Japan, Germany, South Korea and Taiwan are world leaders in nanotechnology as illustrated by Fig. 1.3, showing 19 countries ranked by their research activity over three years [4]. Even though Norway's activity was too small to be considered in this study, The Norwegian Government has the funding and vision necessary to reach prominence in nanotechnology research. NANOMAT (2007–2011) was a project initiated by the government to lay the foundation for such achievements by building cleanrooms and supporting research projects. The project was followed by NANO2021 (2012–2021) and *The Govenment Research Strategy for Nanotechnology 2012–2021* which goal is to reach international levels [5].

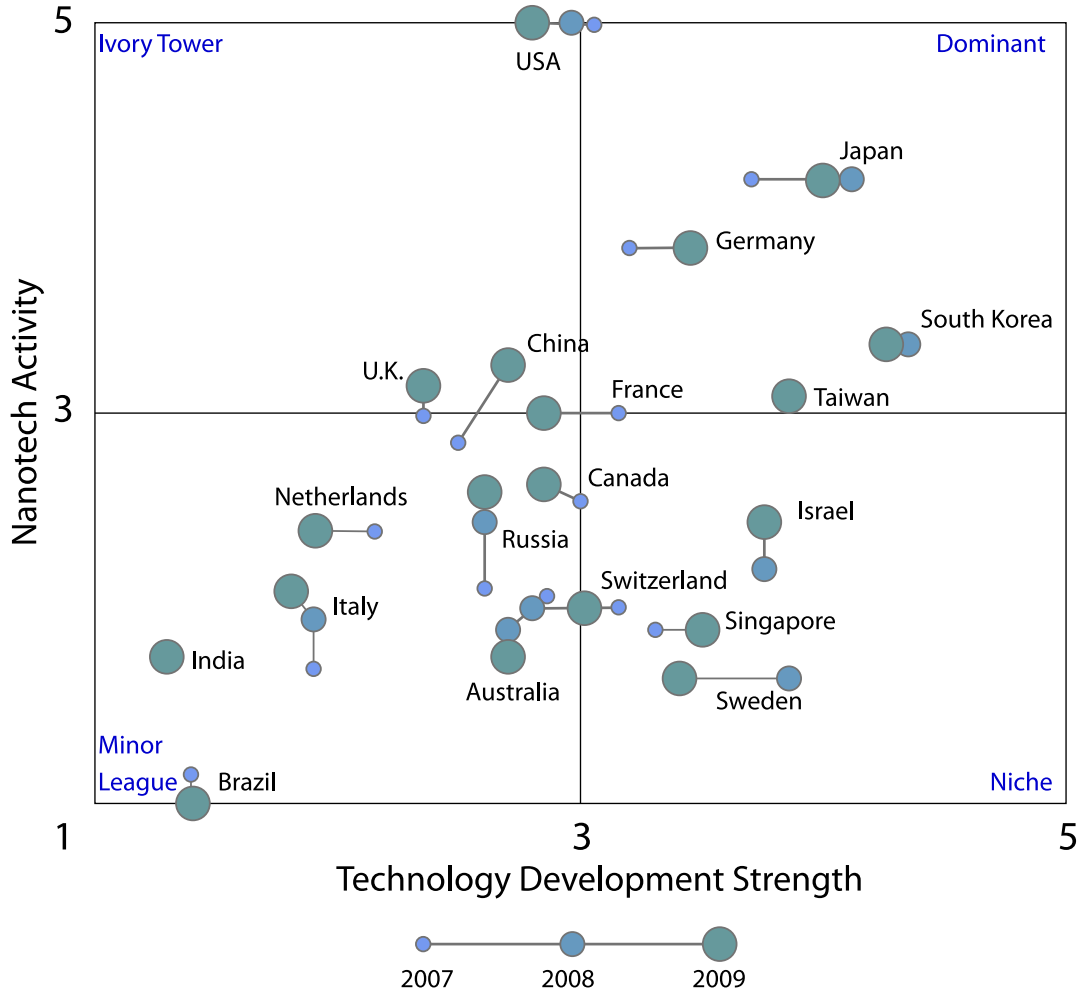


FIGURE 1.3: Diagram ranking the leading countries of nanotechnology by research quantity (y-axis) and quality (x-axis) from 2007 to 2009 [4].

It might seem as a risky operation to initiate product development on such a material, but as the fabrication techniques improve and the production volume increases, the cost is coming down [6, 7]. With the support from the government, any investment may be highly subsidized and economic risks mitigated. The health risk is present, but the science community expects to find types of CNTs to be harmless [8]. There is currently an opportunity to patent extraordinary innovations with government support and low competition. The timing is just right.

This thesis will initiate the development of products by the use of carbon nanotubes in applications of national interest. Norway has long been a master of the sea with its long coastline and large water territories (Fig. 1.4). They employ

some of the most profitable industries in Norway; aquaculture, shipping and offshore oil/gas. I will show how these industries may use carbon nanotubes to hold a competitive edge.

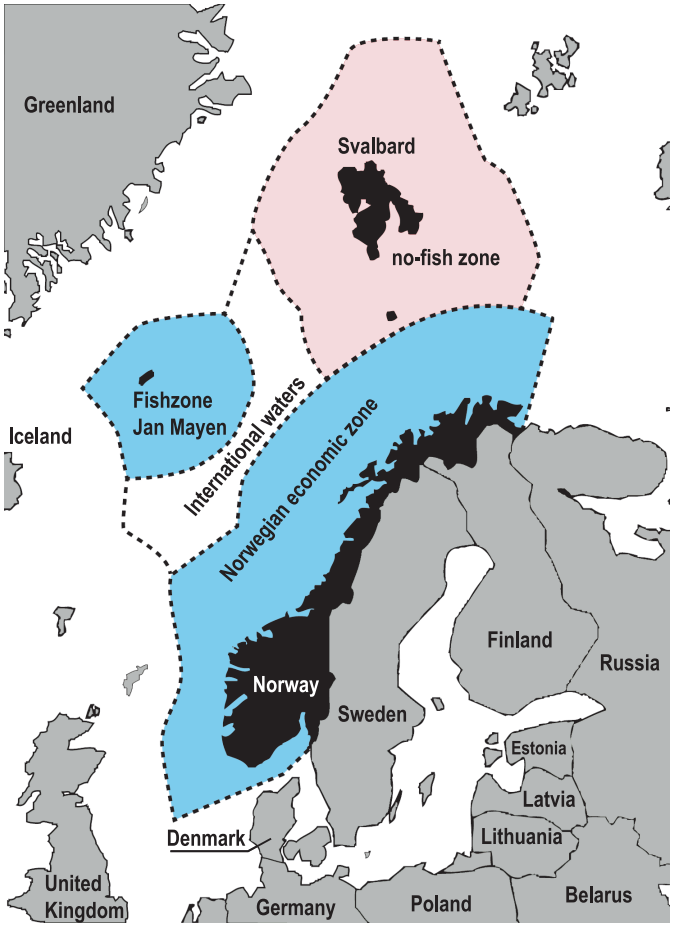


FIGURE 1.4: Water territories ruled by the Kingdom of Norway. Adapted illustration [9].

1.2 Methodology

One may choose among two fundamentally different innovation approaches; *need pull* or *knowledge push* [10]. Need pull (or pull innovation), the most common approach, has the user's need in mind from day one and the product is meant to fill a demand. As illustrated by Fig. 1.5, the innovator knows how the gap looks and pulls the box to fill it. The opposite approach, knowledge push (push innovation), focus on research and development with no clear user in mind. The innovator is much closer to the box so he knows it much better, but he cannot

see the gap. The user is identified after the concept has been developed and the product is pushed into the hands of the user. Several products developed using knowledge push have had enormous success, such as nylon, antibiotics and transistors [10].

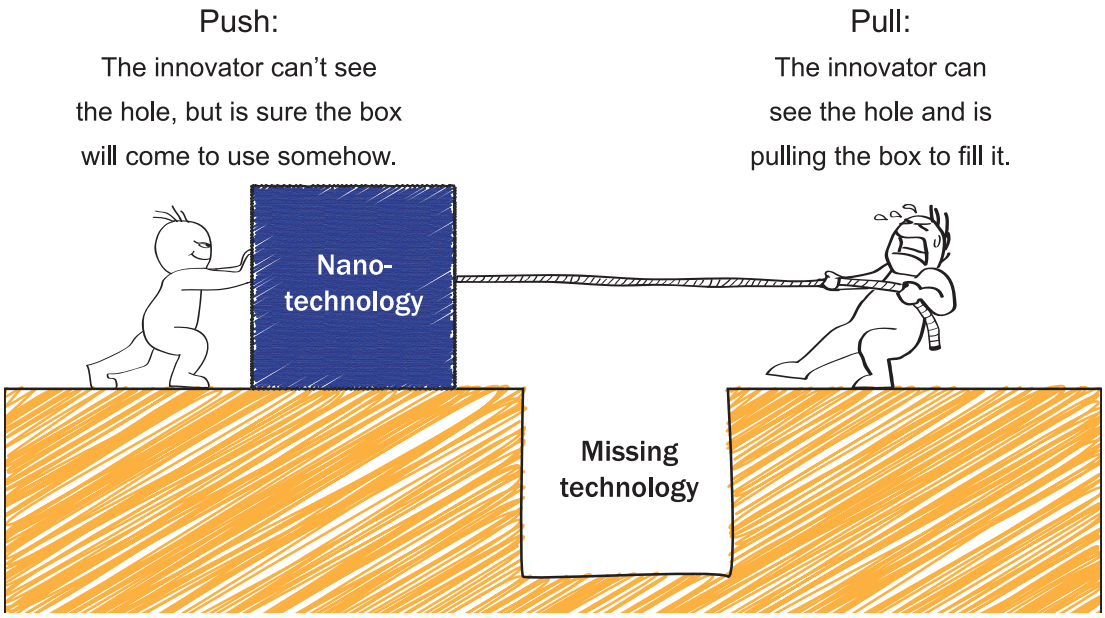


FIGURE 1.5: Illustration of the two concepts of innovation. The pull innovator sees the gap and pulls the box to fill it. The push innovator cannot see the gap, but he knows the box much better.

This project has root in the utilization of a specific technology and material without knowing what the final product will do, hence a knowledge push approach is the best fit. In order for such a project to succeed, the theory of *knowledge and technology transfer* should be applied. The goal is to transfer the technology from the research lab to the right user at the right moment. Several models discuss this process, including the *appropriability model*, the *dissemination model*, the *knowledge utilization model* and the *stage model* [11, 12].

The model chosen for this thesis is the stage model developed by Gibson and various coauthors [12]. Their model was developed for high-tech industries and describes four levels of technology transfer, starting with research findings at the first level and narrowing into commercialization in the fourth as elucidated in Table 1.1. It is quickly recognized that carbon nanotubes are stuck within level II and level III as there is a large amount of research articles, but few business ideas.

TABLE 1.1: Levels of the stage model of knowledge and technology transfer [12].

Level	Characteristic
I - Creation	Individuals and small groups conduct state-of-the-art research and publish results in journals, conferences, etc. No constraints on the research topics and purpose.
II - Sharing	The new potential made by the research is made accessible across intellectual and organizational boundaries attempting to locate an end user.
III - Implementation	The end user and application is located and the potential is implemented into an actual product including manufacturing process.
IV - Commercialization	The product is introduced to the market.

In their research of the *Microelectronics and Computer Technology Corporation* (MCC) in the United States, Sung and Gibson identified four key factors increasing the success of knowledge and technology transfer; communication, motivation, distance and equivocality [12]. Well organized communication channels and motivating incentives will facilitate faster and wider spread of the knowledge. The distance and equivocality should be reduced, i.e. decreasing cultural barriers and reducing the complexity of the knowledge.

This thesis is focusing on sharing knowledge and technology of CNTs and implementing them into applications. The first step will be to collect data from research journals and combine them into a brief review of the material properties (Chap. 2). The properties will then be discussed with a broad specter of people to locate any use of the material (Chap. 3). Once potential applications and users have been identified, concept development and product design will be performed (Chap. 4). The final step is to realize the concept in the lab by making a prototype (Chap. 5). A cost analysis is added to see the market potential (Chap. 6).

Chapter 2

Material Potential

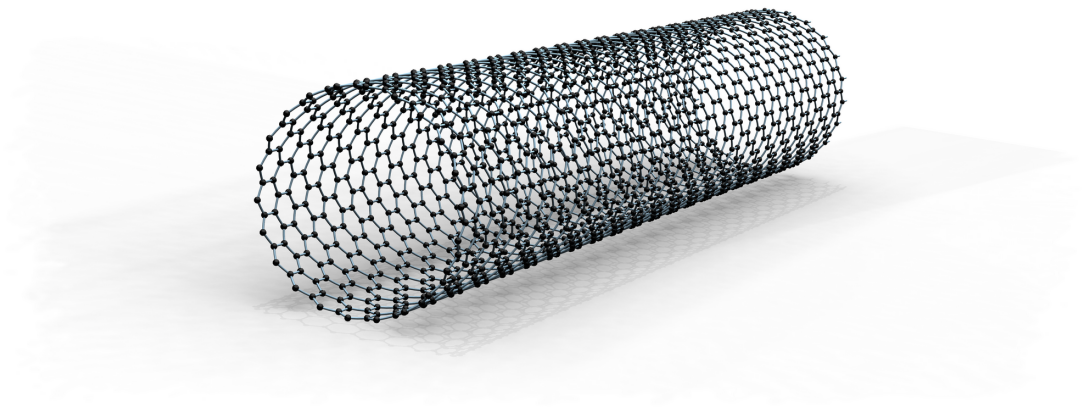


FIGURE 2.1: Schematic of a single-walled carbon nanotube. The diameter vary from 0,5 nm to 2 nm and the length from 10 nm to 1 cm.

The foundation of push innovation is the box of knowledge and technology you build your device upon. Therefore, this chapter will be all about what we currently know about the carbon nanotubes. Material properties such as tensile strength and electrical conductivity are divided into their respective fields of science and shortly reviewed. The second part will explore the states of which you would normally acquire the nanotubes, like CNT powder and CNT yarn. After reading this chapter, you will see the potential of carbon nanotubes to solve material challenges.

2.1 Material Characteristics

Like any other tube, the carbon nanotube (CNT) has a certain diameter and length, in addition to twisting and numerous shells [13]. Tubes with only one shell are called single-walled carbon nanotubes (SWCNTs) and typically have a diameter of 0,5 – 2 nm and a length of 10 nm – 1 cm. Chirality is a term that specifies the twist of the tube and it is expressed by a chiral index (n,m) (also known as chiral integers or chiral indices). The chiral index forms the chiral vector $\vec{C_h} = n\vec{a_1} + m\vec{a_2}$ (lattice vector or roll-up vector), a chiral angle θ and determines the diameter of the tube [14]. The chiral vector represents the line between two nodes on a sheet of hexagons that are connected when rolled up to a tube as seen in Fig. 2.2. The tubes with chiral index (n,n) and (n,0) are special and are called armchair and zigzag tubes respectively. A CNT with multiple shells is called a multi-walled carbon nanotube (MWCNT). A MWCNT with only two shells is called a double-walled CNT (DWCNT). If the CNTs are aligned in either vertical or horizontal direction they are called vertically aligned CNTs (VACNTs) or horizontally aligned CNTs (HACNTs).

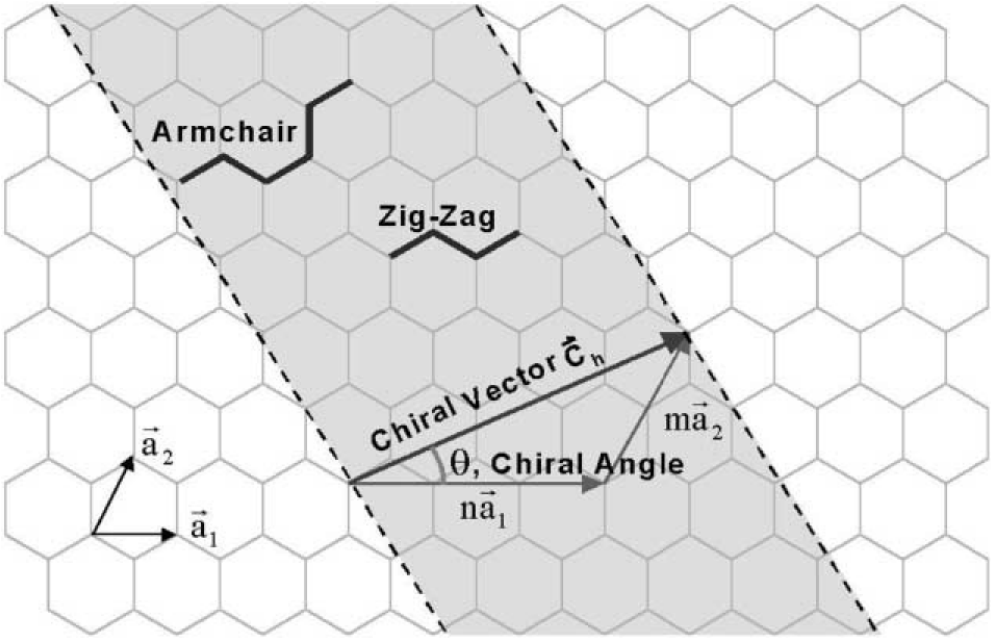


FIGURE 2.2: The sheet of hexagons is rolled up so that the two ends of the chiral vector $\vec{C_h}$ are connected as seen by the grey color. The zigzag and armchair vectors are of particular interest [13].

2.2 Material Properties

It is evident that any material property is dependent on the scale at which it is considered. A well known phenomenon in mechanical engineering is Griffith's criterion of fracture mechanics [15]. He investigated the size-dependence of glass and concluded that as the specimen decreases, the cracks present in the material also decrease, hence the strength increases. As for nanomaterials, the material could have great properties on nanoscale, but the strength diminishes very rapidly once scaled to macroscale. Any claim of ultimate values of properties of nanomaterials should therefore be taken with consideration. Nevertheless, a review of the carbon nanotube properties at the nanoscale follows.

2.2.1 Mechanical

Because the length can be up to seven orders of magnitude greater than the diameter, CNTs happen to fall between two branches of mechanics as seen by Table 2.1. It is too narrow to use continuum mechanics and too long to use molecular dynamics [16]. Simulating the material in a macroscale application complicates even more. The solution is to find a coupling between the molecular dynamics (MD) of atomistic modeling and the finite element method (FEM) of classical continuum mechanics such that it can simulate both crack propagation and structural failure. These models, called multiscale models, vary in several ways including equilibrium condition (force or energy), boundary condition (strong or weak), size of transition region and whether to treat the continuum as linear or not [17].

TABLE 2.1: Time and length scales for mechanical points of view [16].

Branch of Mechanics	Length scale [m]	Time scale [s]
Quantum mechanical analysis	$< 10^{-8}$	$10^{-15} - 10^{-12}$
Molecular dynamics	$10^{-10} - 10^{-6}$	$10^{-9} - 10^{-3}$
Micromechanics	$10^{-6} - 10^{-4}$	$10^{-9} - 10^{-3}$
Continuum mechanics	$> 10^{-3}$	$> 10^{-3}$

Using these multiscale models, CNTs had early predictions of Young's modulus exceeding 1 TPa. Most experiments of strength and stiffness of CNTs are done with a few measurements by microscale equipment and then curve fitted to a simple linear elastic model of continuum mechanics. It is common to use the interlayer spacing of graphite, about 0,35 nm, as the thickness of a CNT shell in the calculations. By chance, Treacy et al. observed in 1996 how the tip of a MWCNT vibrated when heated in a transmission electron microscope (TEM) [18]. They measured the amplitude and fitted it to the amplitude of a vibrating continuous cylindrical cantilever. The calculated Young's modulus was between 0,4 and 4,15 TPa with an average of 1,8 TPa. The validity and accuracy of this and preceding tests are questionable, but they seem to converge around a tensile strength of 100 GPa and a stiffness of 1 TPa [14, 19–22]. The elegant experiment by Peng et al. in 2008 is worth mentioning [14]. The group from Northwestern University made a microscopic testing stage for classical tensile test, stretching a SWCNT until failure. By the stress-strain curves as seen in Fig. 2.3, they could easily detect a tensile strength of about 101,7 GPa (in an interval of 98 – 110 GPa) and breaking strain of about 13%. The Young's modulus was calculated with an average of 1,048 TPa (in an interval of 0,990 – 1,105 TPa).

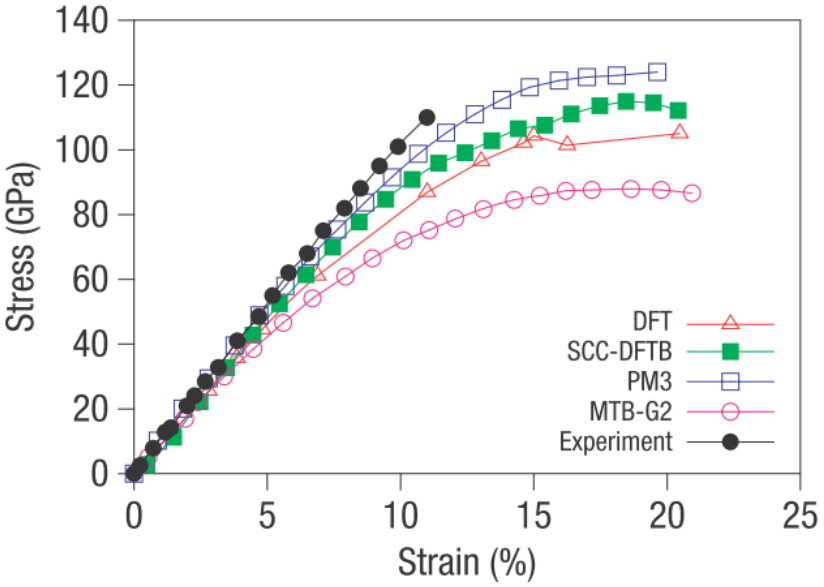


FIGURE 2.3: Stress-strain curve of a SWCNT by Peng et al. Black dots are experimental result, the others are simulations [14].

2.2.2 Electrical

Besides the enormous strength, the CNTs possess an exceptional electrical conductivity. The conductivity of carriers along the material surface is favored by two features; the CNTs 1D structure allowing a straight path and the freely bonded valence electrons forming a delocalized π-band on its surface, similar to metals. The resistivity of CNTs at room temperature are in the range of $10^{-2} - 10^{-6}$ Ωm while silicon and copper have resistivity of $1,00 \cdot 10^{-4}$ Ωm and $1,70 \cdot 10^{-8}$ Ωm respectively (note that lower resistivity means higher conductivity) [23, 24]. Obviously the CNTs should be aligned in the direction of the current as done by Salahuddin et al. when they compared copper and CNT (Fig. 2.4) [25].

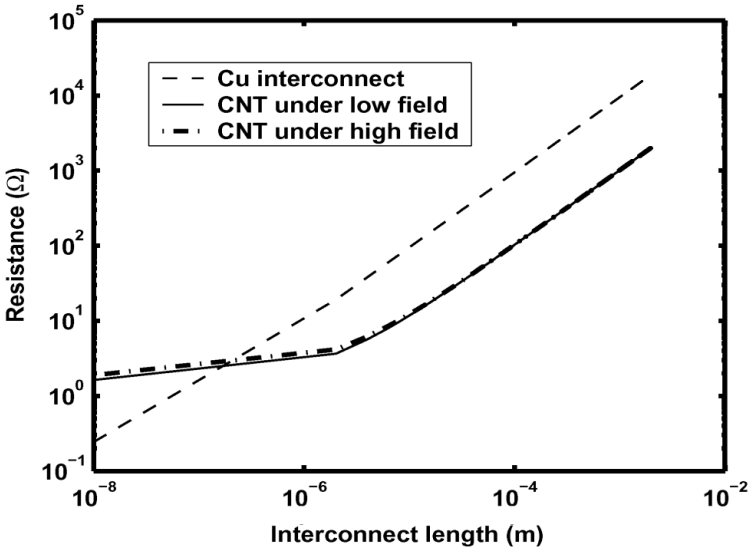


FIGURE 2.4: Resistance at short lengths of copper wire compared to 4000 parallel CNTs, both having the same cross sectional area. CNTs outdo copper at lengths greater than 1 µm [25].

Experiments have shown a clear correlation between the conductivity and the twisting of the tube, hence the chiral index (n,m) defines the band gap and whether the CNTs are metallic or semiconducting. If the chiral index is known, it is easy to test for conductivity by Equation 2.1. If the answer is a multiple of three, the CNT is considered metallic due to a small band gap, else it is semiconducting. On the other hand, if the conductivity is known, the chiral index can be determined. The armchair tubes (n,0) have no twisting to inhibit the conductivity and are therefore truly metallic, while the zig-zag tubes (n,n) can be both metallic and

semiconducting. As the MWCNTs can hold tubes of different chiralities, their electrical properties are very complex.

$$2n + m = \begin{cases} \text{multiple of 3} & \Rightarrow \text{metallic} \\ \text{else} & \Rightarrow \text{semiconducting} \end{cases} \tag{2.1}$$

2.2.3 Thermal

The great electrical conductivity is accompanied by a good thermal conductivity with reports up to one order of magnitude higher than copper at room temperature [26]. Experiments have shown the thermal conductance at very low temperatures to be without resistance (one-dimensional and ballistic) due to a longer photon mean-free path than the length of the nanotube [27]. At higher temperatures, the mean-free path shortens and the defects start obstructing, lowering the thermal conductivity as seen in Fig 2.5. There is still a lot of research to be done in this field, but so far the results are very promising. At room temperature, the thermal conductivity of CNTs are measured well beyond 3 000 W/m-K [28]. For comparison, diamond has a thermal conductivity of 2 000 W/m-K and is one of the best heat conducting materials known to date [29]. This makes CNTs a great candidate for thermal management applications.

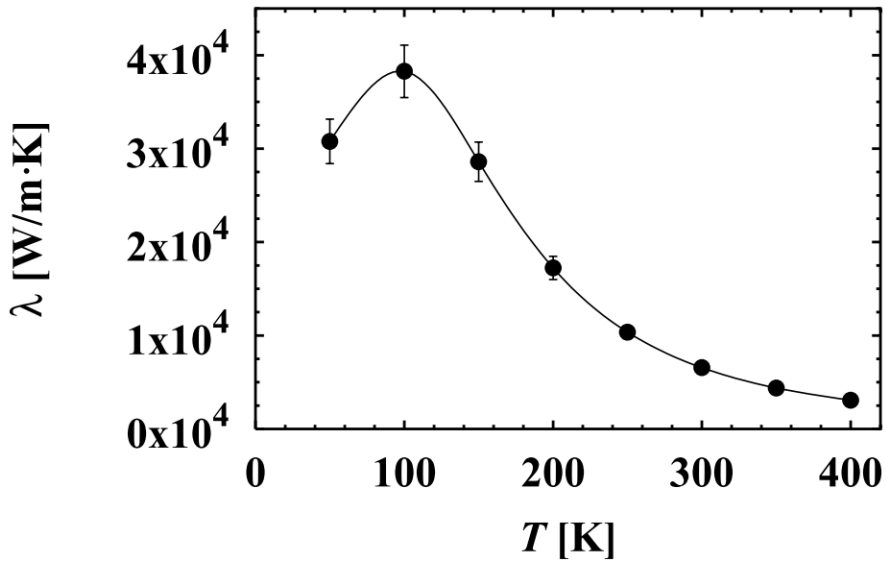


FIGURE 2.5: MD simulation of the thermal conductivity of a (10,10) isolated carbon nanotube with respect to temperature [27].

2.2.4 Chemical

A SWCNT without any defects or end caps can be considered a chemically inert macromolecule. The strong covalent carbon-carbon bonds make the atoms difficult to separate, but the tubular and twisted structure adds extra stress which reduces the stability [29]. The smaller the diameter and the more twisted, the more strain and more reactive the CNT. Simulations have shown SWCNTs to be more stable than fullerenes, MWCNTs more stable than SWCNTs and graphite more stable than MWCNTs.

Despite its strong bonds, SWCNTs will break down when sonicated with strong oxidizing agents such as NHO_3 and H_2SO_4 or strong organic solvents like dimethylformamide [30]. Defects and tube ends are weak spots to which failure can initiate with complete amorphisation as the final result.

The most common defect is the Stone-Wales defect, also known as the pentagon/heptagon- or 5/7 defect, that may develop during synthesis or arise due to heavy loading on the carbon bonds [29]. It is believed to be one of the main contributors to the ductile behavior of CNTs. If an armchair CNT is stretched, MD simulations have indicated bonds to rotate creating two pentagons and two heptagons as illustrated by Fig 2.6 [13].

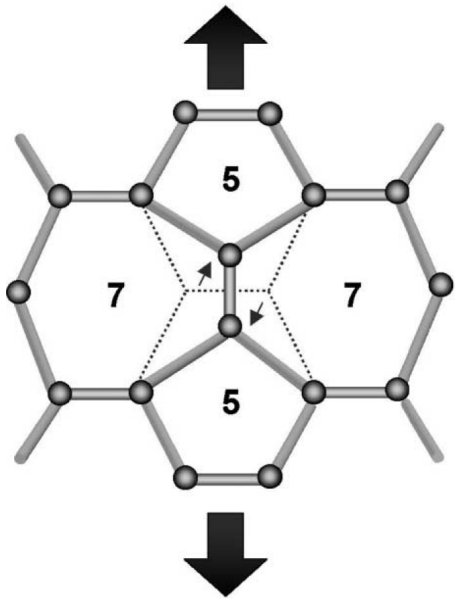


FIGURE 2.6: Schematic of a Stone-Wales defect in an armchair CNT. The applied load makes the center covalent bond rotate creating two pentagons and two heptagons [13].

In order to break down a CNT by heat alone in an argon atmosphere, temperatures well above 2000 °C are needed. Studies show that SWCNTs coalesce (enlarging their diameter) at 1600 °C and eventually transform into MWCNTs at temperatures above 2200 °C [31]. Double-walled CNTs are more stable than SWCNT and keep their diameters until 2100 °C before they transform into MWCNTs at 2200 °C [32]. At temperatures above 2300 °C, the MWCNTs start fragmenting into amorphous carbon.

2.2.5 Biological

The great stability of CNTs is alarming the scientists working on biological properties . Parallel to the exploration and fabrication of CNTs, mice are being tested for asbestos-like behavior of CNT contamination [33]. CNTs are often put alongside asbestos because they're both fibrous materials with high tensile strength, high thermal stability and resilient to chemical solvents (Fig. 2.7a). If the harsh defense of the human body can't get rid of the alien material, it will stay in the body and may cause serious harm.

Asbestos is dangerous because it slips between the human body's two defense lines [34]. The first is the *tracheobronchial muscociliary escalator*, also known as nasal mucus, that capture particles and carry them away. The asbestos fibers are too small and too slick to be effectively captured, hence they slide through and into the lungs. The second defense is the *macrophage* cells in the lungs that ingest and destruct foreign substances. Asbestos, with its length and biopersistence is too long for the macrophage to ingest and too stable to destroy. As a result, the asbestos will stay in the lungs and release free radicals that damage tissue and DNA as well as inducing inflammation; perfect growing conditions for tumor and *mesothelioma* cancer [35].

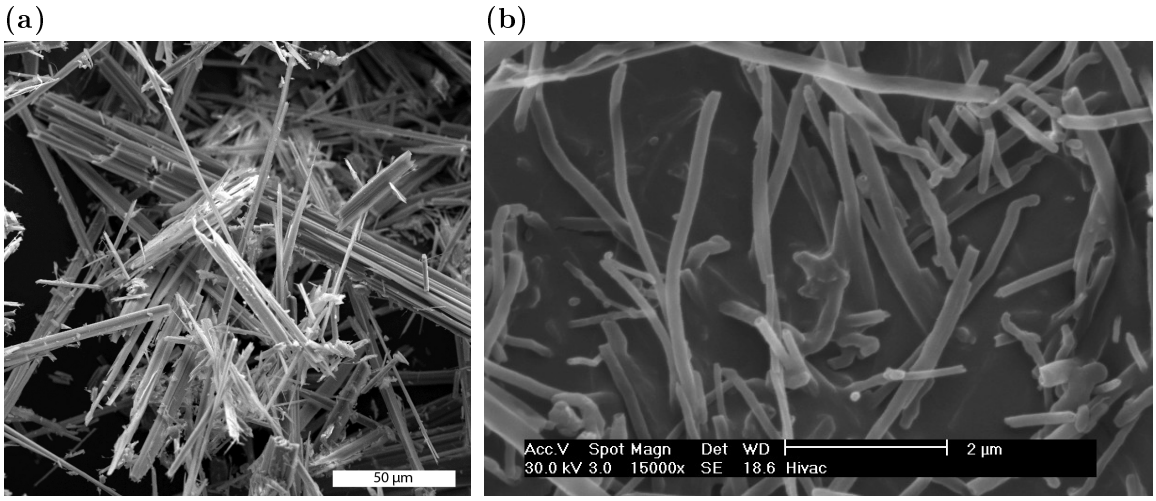


FIGURE 2.7: Comparison of physical structure. **(a)** SEM image of Anthophyllite asbestos fiber. Scale bar: 50 µm [36] **(b)** SEM image of asbestos-like carbon nanotubes. Note, scale bar: 2 µm [37].

The fear is that CNTs, with their comparable length and chemical stability as illustrated by Fig. 2.8, are as toxic as asbestos. They should therefore be treated with great care to avoid inhalation. However, the CNT properties change dramatically by length, chirality, number of shells, agglomeration, etc., hence there might be good CNTs and bad CNTs. Research groups are now conducting long run *in vivo* experiments on mice exposed to CNTs. Luckily they are giving conflicting results for us to distinguish the good CNTs from the bad [8, 38–40].

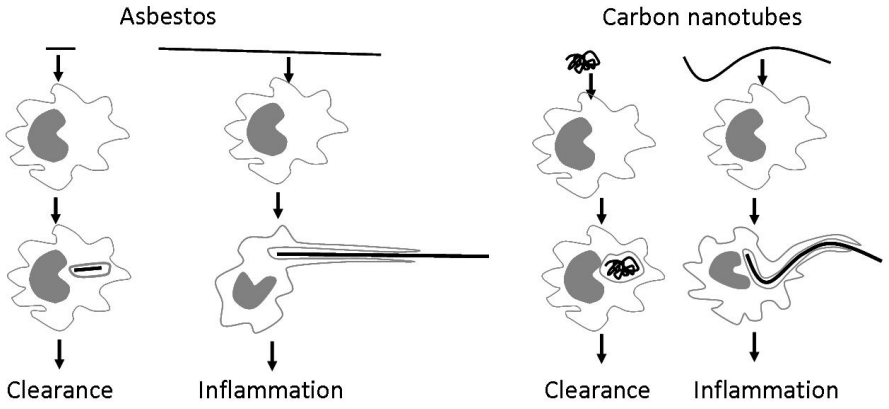


FIGURE 2.8: Schematic of a macrophage cell trying to ingest different asbestos and CNT structures. The macrophage is unable to ingest long fibers resulting in inflammation [33].

2.3 Material Arrangements

After synthesis, the tubes may be refined into several arrangements and the development of any application should originate from one of these. This section will review the most common macroscale CNT arrangements.

2.3.1 Dispersed in Liquid

Carbon nanotubes are extremely resistant to wetting and tend to agglomerate and entangle themselves together in a dense network [41]. Depending on the application, this can either be desired or annoying, but either way it is necessary to know what it takes to separate them. Clearly this involves liquid dispersion where two methods are common; mechanical by ultrasonication or chemical by solvents. Ultrasonication is fast and efficient, but has a tendency to fragment and destroy some of the tubes as well as only being temporary. A chemical solvent is needed to keep the tubes separate and usually involves alternation of the CNTs surface energy or attaching a water-soluble molecule to its surface or ends. Solvents like sodium dodecylsulphate (SDS) and sodium dodecylbenzenesulphonate (NaDDBS) are most commonly used [42, 43], but they may also harm the nanotubes and change their properties.

DNA has proven to be particular selective in wrapping around specific carbon nanotubes as illustrated by Fig. 2.9 [44]. The wrapping makes the CNTs suspendable in aqueous solution as well as making them negatively charged. By adding a range of different DNA sequences that attach to different chiralities, the tubes will have different electric charges based on their chirality which further simplifies sorting. Due to the high cost of DNA, polymers have been investigated as an alternative [45].

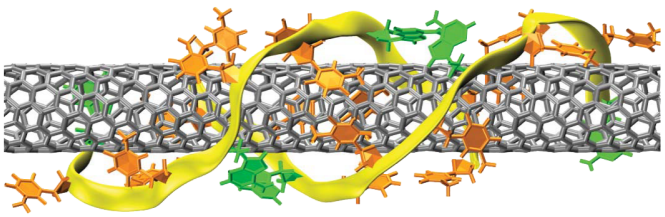


FIGURE 2.9: Schematic of a DNA string wrapped around a (8,4) carbon nanotube [44].

Dispersed in a liquid, as in the bottle in Fig. 2.10a, is the most common way of purchasing CNTs. They are usually mixed with a surfactant followed by a short ultrasonication. Purification and sorting have also been performed to remove undesired amorphous carbon, catalyst remains, etc. The dispersed CNTs also go by the name of CNT ink. Because many applications have strict requirements to the electrical conductivity, bottles of only metallic or only semiconducting tubes may be bought.

FIGURE 2.10: Bottles of various arrangements of CNTs. **(a)** A bottle of 25 mg highly purified SWCNTs dispersed in 100 ml deionized water and ionic surfactants [46]. **(b)** A bottle of SWCNT powder with lengths 5 – 10 µm [47] **(c)** A bottle of 25 mg SWCNT powder, highly purified and stamped into a thin sheet [46].

2.3.2 Dried Powder/Sheet

Drying the solution of CNTs produce an entangled powder as seen in Fig. 2.10b. The sample is lighter, but CNT powder is inconvenient due to the hazards when airborne. It is therefore common to stamp the powder into a sheet, also known as buckypaper as seen in Fig. 2.10c. Buckypaper may be dissolved again by the techniques mentioned in section 2.3.1. Larger sheets by the meter and with thickness down to 20 – 30 µm are available from Nanocomp Technologies [48]. The sheets are highly entangled and have no alignment.

2.3.3 Attached to Substrate

Some synthesis techniques yield CNTs attached to a substrate with varying degree of alignment. Most common is growth of CNTs by chemical vapor deposition

(CVD) either along the substrate plane or as a forest of vertical tubes seen in Fig. 2.11. They require no post-treatment after synthesis, the tubes are organized and aligned and finally, the tubes stick to the substrate. They stick well enough not to fall off, but are also easy to pull off when called for. The current price for a 1 cm by 1 cm silicon wafer filled with VACNTs delivered by Aldrich Materials Science is about 10 880 NOK [49].

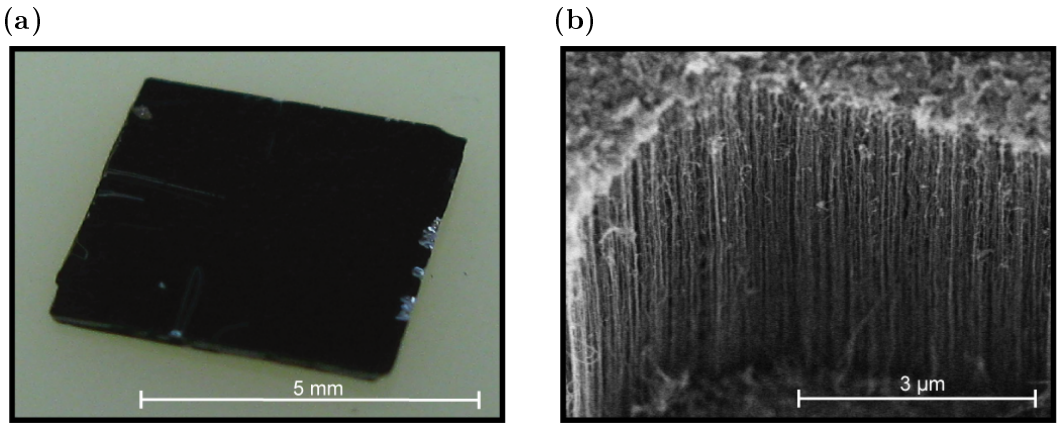


FIGURE 2.11: **(a)** Photograph of wafer containing VACNTs grown at NTNU Nanolab. **(b)** SEM image of VACNTs at 18 000 times magnification [50].

2.3.4 Yarn

Many of the CNTs excellent properties are only true in the axial direction. As the longest grown CNT is no more than 20 cm [51], the CNTs have to be joint together somehow to extrapolate the properties to macroscale. The most common method is making a yarn with the CNTs aligned as much as possible. The CNTs may be spun into a yarn in four different ways [52]:

Spinning from CNT Solution The CNTs are dispersed in a liquid and injected into a spinning bath of another solvent. The CNTs re-agglomerate and form a yarn which is pulled out of the bath, washed and dried.

Spinning from CNT Array A small tape is attached to the end of an array of VACNT and pulled out. The CNTs then follow in a sheetlike fashion before twisted into a yarn.

Spinning from CNT Aerogel The yarn is formed during CNT synthesis in a vertical furnace. A catalyst is injected at the top. As the catalyst flow

downward in the furnace, CNTs form and entangle themselves together. A spool at the bottom collects the yarn.

Twisting or Rolling CNT Sheet A thin sheet of entangled CNTs is sliced from a thicker sheet and rolled to form a tube.

Miaudet et al. found their CNT yarn to have a tensile strength up to 1,8 GPa, a high toughness and low weight [53]. Other studies have shown the yarn's strength to be independent of any knots tied on it [54]. Furthermore, CNT yarn has been reported to absorb water by swelling. Baughman and coworkers experienced a swelling to a diameter of 200% its initial size [55].

The current top producer of CNT yarn is Nanocomp Technologies with a range of clients including Boeing, the U.S. Army and NASA [48]. They charge about 17 – 29 NOK/meter for their 50 – 75 µm diameter one ply yarn [56].

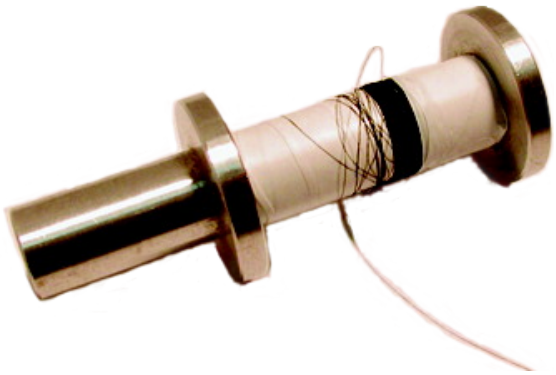


FIGURE 2.12: Photograph of 10 m CNT yarn with a diameter of 30 µm winded on a spool [53].

2.3.5 Fabric

The CNT yarn may be woven into a fabric by regular textile techniques. The fabric is highly versatile, combining the CNTs one-dimensional properties with a two-dimensional structure. A film of CNTs may also be drawn directly from a CNT array as seen in Fig. 2.13. Zhang et al. had great success in making 5 cm wide, 50 nm thick and meters long fabric using this technique [57]. The fabric showed superhydrophobic performance by supporting drops of water without wetting. CNT fabric has also shown behavior of letting oil pass through while stopping water, known as superoleophilicity and superhydrophobicity respectively [58, 59].

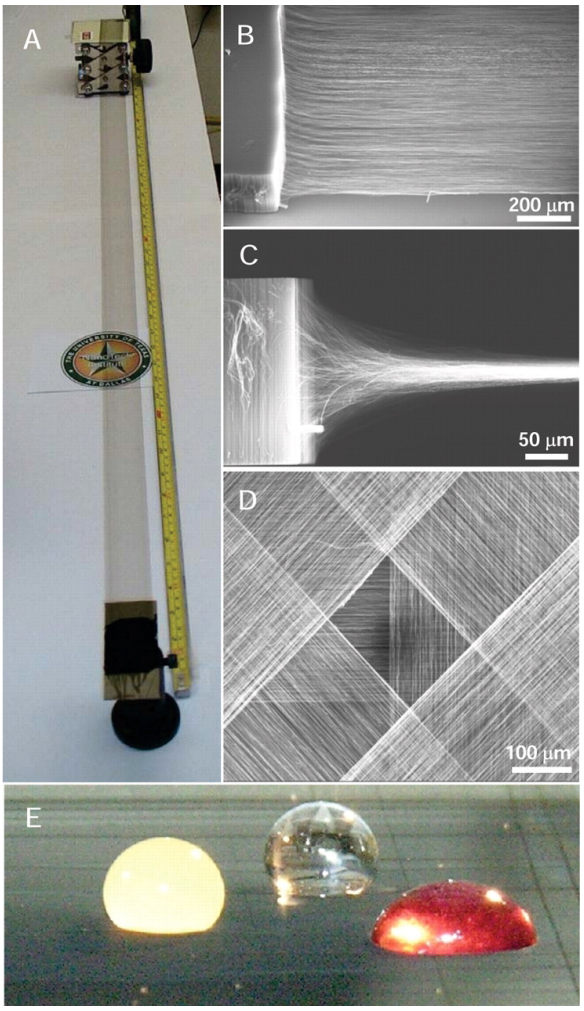


FIGURE 2.13: Figure 1 from paper on CNT sheet by Zhang et al. [57]. **A** Photograph of a 3,4 cm wide fabric drawn from a VACNT array. **B** SEM image of fabric being drawn. **C** Cross section SEM image of fabric being drawn. **D** SEM image of overlaying CNT fabrics. **E** Photograph showing the fabric's low wettability with (f.l.) drops of water, orange juice and grape juice.

Chapter 3

Locating Applications

FIGURE 3.1: M/S Stril Commander. Norwegian Tug/Supply/Rescue Vessel [60]

This chapter report how ideas developed through communication with Norwegian companies as encouraged by Gibson's stage model [12]. They should be made aware of the new possibilities the material bring, followed by motivation and brainstorming. The search focused on three main industries; aquaculture, shipping and offshore oil/gas. An aquaculture net cage and hydraulic oil drier are among the potential business ideas that emerged.

3.1 Approach

Several firms and organizations were contacted to discuss problems they faced with regards to material properties in the maritime environment. The goal was to locate applications, users and partners and the search was divided into aquaculture, shipping and offshore oil/gas. Furthermore, an example of a semifinished product was presented in order to establish CNTs as a macroscale product, not a nanoscale spectacle. CNT yarn was chosen because it is easy to comprehend. To encourage and enlighten the representatives, a flyer was sent out by email (Fig. 3.2). Full size flyers found in supporting material online and magnified offshore oil/gas flyer found in Appendix A.

FIGURE 3.2: Flyers sent out to attract attention and ideas from the industry.

Companies being reluctant and skeptic were introduced to Zyvex Marine. The startup company is already building marine vessels out of carbon fiber/CNT composite as the one in Fig. 3.3 [61]. They mix CNTs into the resin, but are using carbon fiber as the main load bearing constituent. Their utilization of CNTs is at a bare minimum, though this project aims to exploit more of the CNT's properties.

FIGURE 3.3: 57feet, long range prototype boat (LRV-17), made of carbon fiber/CNT composite by Zyvex Marine [61].

3.2 Business Ideas in Aquaculture

Aquaculture refers to the marine fish farming industry in Norway producing in excess of 1,1 million tons of seafood worth about 50 billion NOK in 2012 [62, 63]. The fish, mostly salmon, is farmed in submerged net cages as seen in Fig 3.4. The farms, located all along the Norwegian coast, sell fish worldwide, making Norway the second largest seafood exporter in the world. The industry has a good focus on sustainability and several issues in need for improvement have been identified.

FIGURE 3.4: Picture of a fish farm in Norway showing only the floating collar of the net cages [64].

3.2.1 Fish Lice

Aquamedicine Biologist Nils Fredrik Vestvik at Aqua Kompetanse AS was interviewed on the problems faced by the fish farming industry [65]. An issue of great concern is the spread of fish lice, a parasite harmful for the well-being of the fish and therefore illegal to ignore. The lice are currently being controlled by vaccinating the fish, but as the lice are evolving, they become resistant to the vaccines. Attempting to functionalize CNT-yarn for such an application is probably a little bit far-fetched.

3.2.2 Mooring Plate

Situated in Trondheim, Aqualine is a well established supplier of fish farming equipment ranging from floating collars to mooring systems [66]. Their 30 years of

experience have culminated to a very short catchphrase; strength counts. Through a meeting with Noralf Rønningen, their Project and Development Manager, strength was indeed the most important property. The equipment in a fish farm needs to withstand large and fluctuating strain in an extreme environment, well illustrated by Fig. 3.5.

FIGURE 3.5: Aqualine fish farm under harsh weather conditions [66].

The mooring plate of a fish farm was identified as critical and in need for improvement. The mooring plate is used to combine mooring lines stretched in different directions below the net cage, balancing out the forces and securing the farm to the ocean floor. The current plate used is a solid piece of galvanized steel as seen in Fig. 3.6. It is heavy, giving high cost and complicating installation. A solution could be to replace the mooring plate with a wind/knot of CNT yarn.

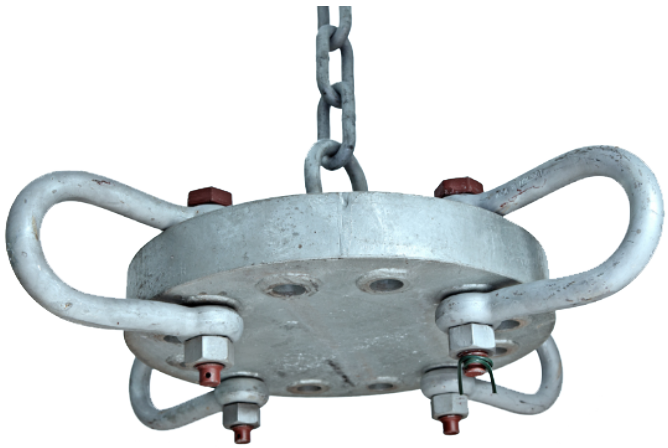


FIGURE 3.6: Aqualine mooring plate used in fastening the farm to the ocean floor [66].

3.2.3 Net Cage

A problem area discussed with both Vestvik and Rønningen is the net cage that surrounds the fish keeping it from escaping the farms as seen in Fig. 3.7. The net is usually made by nylon due to its low cost and perseverance in salt water. The problem with nylon is the strength; it is too weak and may easily rupture. Suppliers are now looking into replacing nylon with strong polymer fibers such as Dyneema.

The net cage also has a problem with algae clogging the net causing oxygen deficiency. The fish farmers need to clean the net regularly, a task often involving submerged jet water washing by divers or ROVs. The task is very expensive and fish farmers would be most interested in a net with antifouling properties that do not let algae to grow.

Carbon nanotubes yarn is strong and non corrosive, hence a potential replacement for nylon. Its chemical stability and hydrophobicity may give antifouling abilities as well.

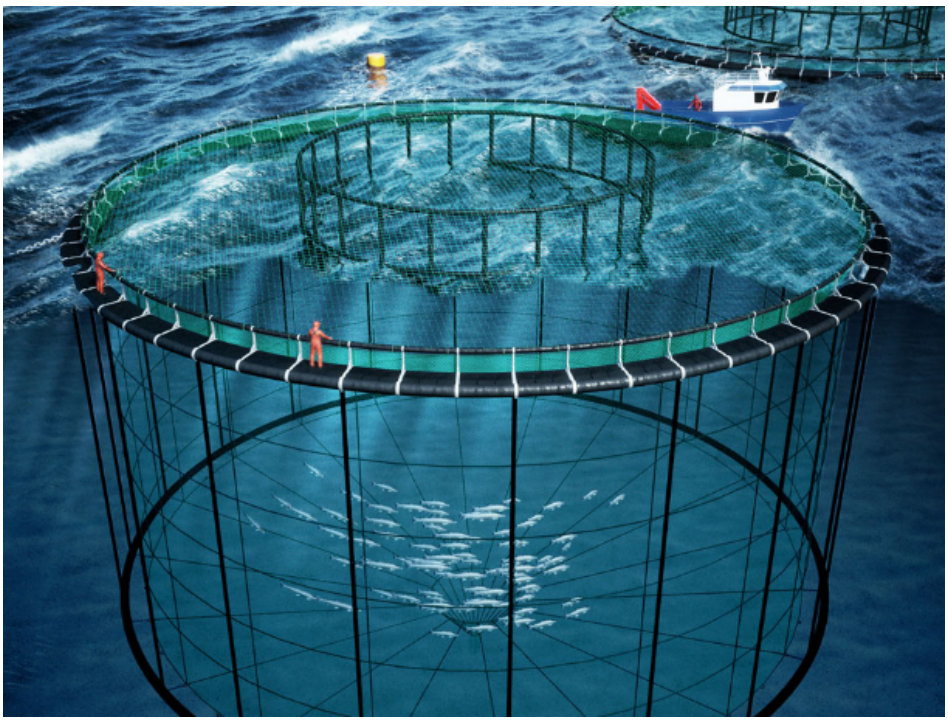


FIGURE 3.7: Illustration showing the order of size of a typical net cage. The amount of fish is not representative [66].

3.3 Business Ideas in Shipping

Norway has a history of shipping stretching from Viking longships to high-tech offshore supply vessels (Fig. 3.8) [67]. The industry employs more than 100 000 people in shipping companies, shipyards, suppliers, services, etc., with a value exceeding 150 billion NOK [68]. Success is not measured by the amount of natural resources extracted, but by the quality and availability of the service provided despite extreme harsh environments. It may well be one of the most challenging industries from a material science perspective.

FIGURE 3.8: Illustration of a Polarcus research vessel designed for operations in arctic waters, made by Ulstein Group [69]. The bow, known as X-BOW, is supposedly inspired by Viking longships [70].

3.3.1 Ropes

Like the use of CNT yarn in net cages, it may be used in tugging and hawser ropes (Fig. 3.9). Offshore & Trawl Supply AS located just outside Ålesund is a well established manufacturer of ropes made of synthetic fibers [71]. Their strongest ropes made of Dyneema fiber have diameters ranging from 6 mm to 350 mm. Fiber ropes have received increasing attention to replace steel chains at low depths and where there is a risk of hitting equipment with the lines. To make CNT yarn attractive to make rope, the tenacity (tensile strength per weight) should be proved at least as high as Dyneema and not be too expensive.

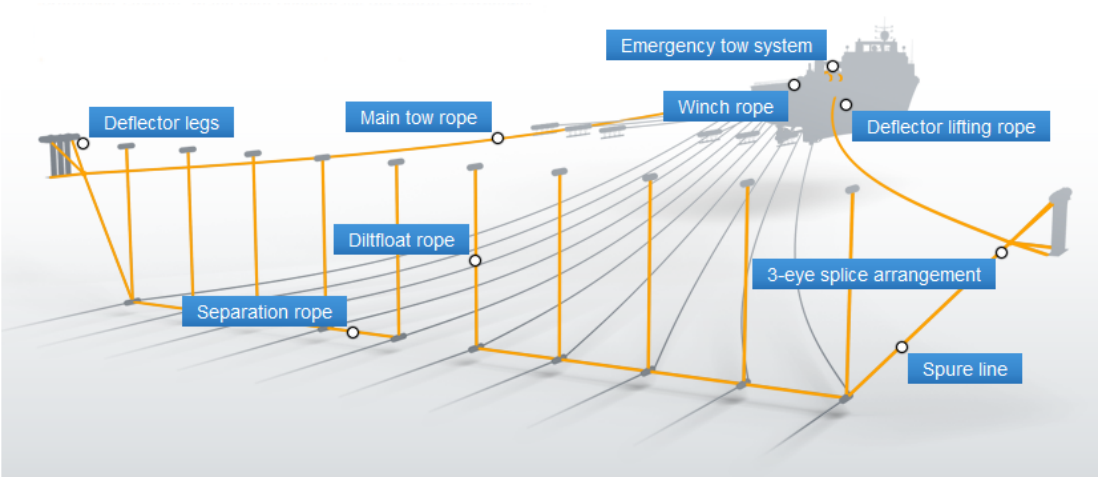


FIGURE 3.9: Illustration showing the large amount of ropes used in seismic operations [71].

3.3.2 HVAC

Novenco Marine & Offshore A/S is a Danish firm and one of the world's leading suppliers of heating, ventilation, air-conditioning and refrigeration solutions for merchant ships and offshore vessels [72]. The HVAC systems typically suck in very humid air, run a heating/cooling process and distribute the air around the ship. As ships often travel across varying climate, the operating conditions of the HVAC systems change frequently, putting a high strain on the components.

CNTs might be suitable for ventilation systems due to their high thermal conductivity and corrosion resistance. Furthermore, the reports on CNT yarn swelling by absorbing water could be useful. A brand new idea will be to use CNT yarn as desiccant in a thermal wheel used in energy recovery heat exchangers. However, this will put the CNTs directly in the ventilation and because there are a lot concern about the health risk of airborne nanomaterials, the idea will likely be turned down.

3.3.3 Thrusters

Located in Molde, Brunvoll AS manufacture, mount and service thrusters on ships typically used for maneuvering ships in tight spaces (Fig. 3.10) [73]. When operating the thrusters, vibrations are inevitable and components will be subject to fatigue. Because CNT yarn has a high toughness, it is believed to be able to

absorb more energy and give components longer fatigue life. Specific components of the thrusters to improve have not been identified.

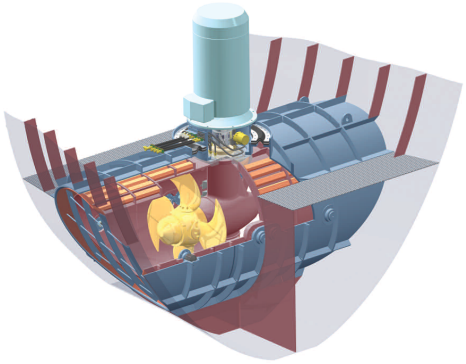


FIGURE 3.10: Illustration of a low noise tunnel thruster made by Brunvoll [73].

3.4 Business Ideas in Offshore Oil/Gas

For more than 40 years, Norway has extracted oil from the continental shelf bringing in immense amount of capital. Today there are 76 fields in production ranking Norway as the fourteenth largest oil producer and the sixth largest gas producer in the world (2011) [74]. It is certainly a matter of national interest as the entire petroleum sector represents more than 23 per cent of the national value creation. There are about 50 Norwegian and foreign companies operating on the Norwegian continental shelf with Statoil as the leading one (Fig. 3.11). In addition, a large amount of suppliers are spread out along the coast.

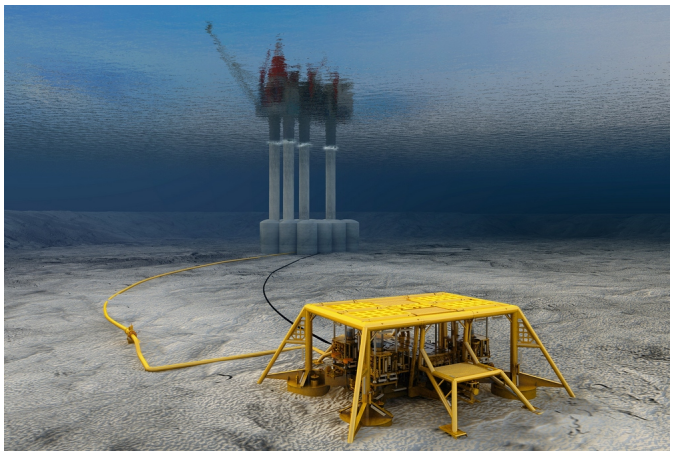


FIGURE 3.11: Illustration of a subsea installation at the Visund South reservoir connected to the Gullfaks C platform operated by Statoil [75].

3.4.1 Buoyancy Body

Through a meeting with Statoil employee adjunct professor Mons Hauge, some of the current material challenges of Statoil were discussed. A currently unsolved issue of Statoil is buoyancy bodies. When lowering equipment down to low depths, the weight of the equipment and lines induce high strain on the vessel. A floating body attached to the equipment is a proposed solution, but balancing the high external pressure with thick steel walls makes the body too heavy. Maybe aligned CNTs in a sandwich structure could be used to support the body on the inside, keeping it from collapsing.

3.4.2 The Arctic Challenge

Professor Morten Karlsen, head of Statoil's Arctic Technology Research Program showed great interest in exploring new materials in their arctic operations. As in Fig. 3.12, equipment quickly becomes covered in ice, making it impossible to operate valves and cranes. Furthermore, construction materials may pass over the ductile-to-brittle transition region seriously decreasing the fracture toughness [76]. Lastly, a high thermal elongation coefficient may cause buckling or gaps, especially when doing start/stop operations giving temperature variations.

According to Prof. Karlsen, CNTs have already been discussed as a solution. By adding CNTs to paint, the hydrophobic properties may be utilized to repel ice. Statoil has also looked into the possibility of adding CNT to rubber to make it more durable and less temperature dependent.

FIGURE 3.12: Photography of equipment completely covered in ice [77].

3.4.3 Oil/Water Separation

There are several uses for equipment that separate oil and water in oil refinement, wastewater treatment, oil spill cleanup and bilge water treatment. Moreover, the presence of water in lubricating or hydraulic system advocate a range of problems including corrosion, reduced lubricity and formation of ice crystals at low temperatures [78]. By installing an oil dryer (water remover) onto the hydraulic system, maintenance is reduced and money saved. A filter of CNT fabric letting oil but not water pass through may be a very profitable business idea. Another approach would be to such up oil using the CNT sponges that have already shown their appearance in scientific journals [79].

3.5 Opportunities To Pursue

Two of the proposed business ideas have been picked out for further development. The concepts should utilize the properties of CNTs, look economic or environmentally feasible and preferably be unique of its kind.

The net cage for fish farming has been chosen because it employs many of the CNT's properties. The combination of high strength, anti-fouling properties and long lifetime makes it ideal for such an application. Also, it is definitely an unique idea.

The second concept is oil drying; removing water contamination from oil in hydraulic and lubricating systems. If succeeded, it would be very profitable with customers in all kinds of industries.

Chapter 4

Concept Development

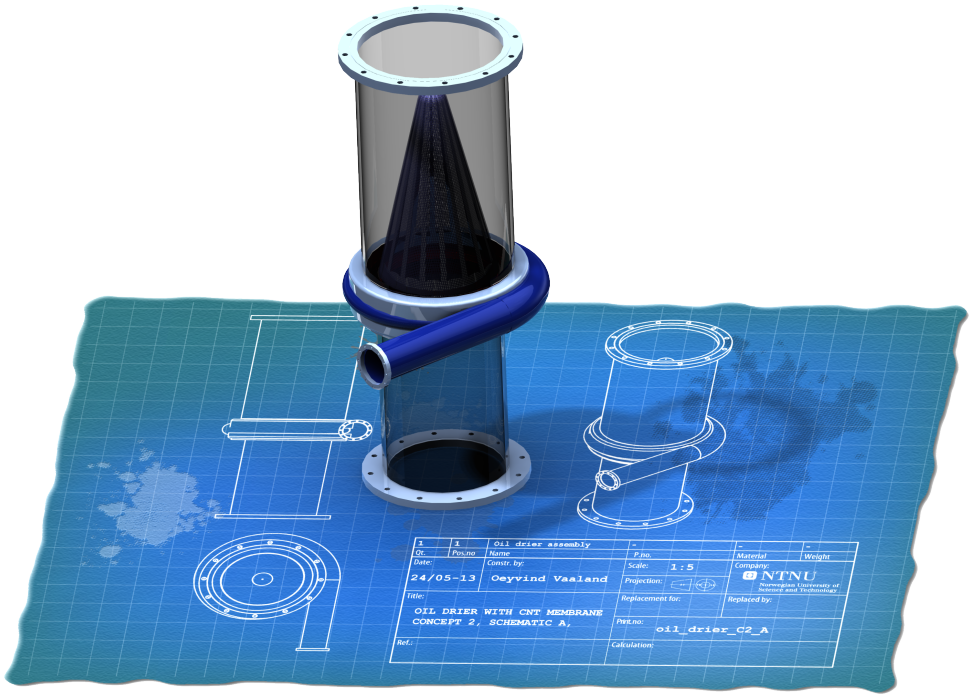


FIGURE 4.1: CAD model of oil drier assembly.

The aquaculture net cage and hydraulic oil drier exploit the extraordinary properties of CNTs in maritime environments and have been selected for further development. This section will study issues with current solutions, look at alternatives and determine whether the CNT solution is viable. Comparison with alternative polymer fibers has been done for the net cage and CAD modeling has been done for the oil drier.

4.1 Net Cage of CNT Yarn

The fundamental function of the net cage is to keep the fish from leaving the farm as well as keeping predators from entering. It is composed of a mesh made with carefully defined openings such that the strength is high and the water flows through easily. A net cage typically has a cylindrical shape, is 50 m in diameter, 20 – 50 m deep and has a narrowing in the bottom as seen in Fig. 4.2.

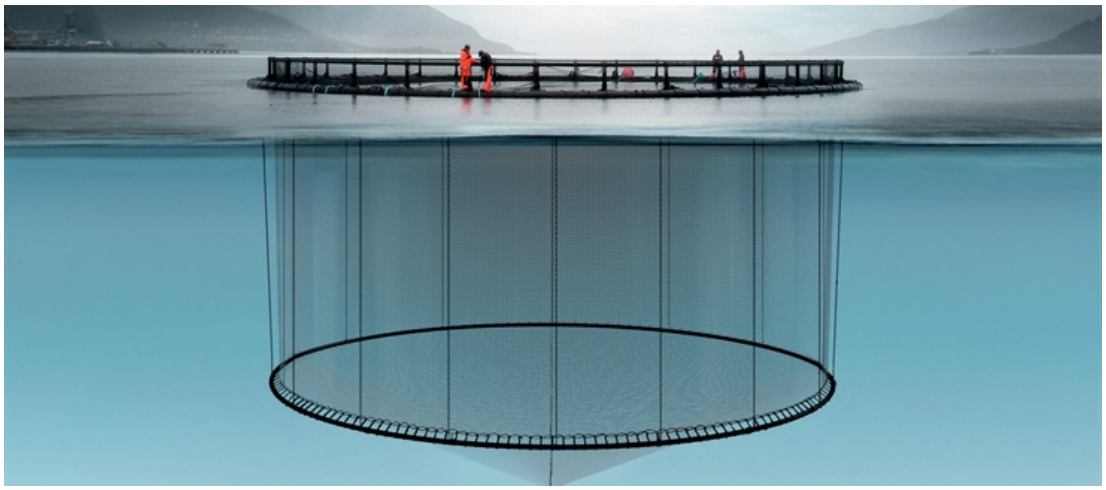


FIGURE 4.2: Illustration of a net cage. The top ring on the surface is called a floating collar, the horizontal submerged ring is called bottom rope and the vertical ropes in between, holding the mesh, are called vertical ropes [80].

The new idea is to replace the twine material of the mesh (usually nylon) with CNT yarn. It is expected this will increase the strength, reduce the need for maintenance and give the net cage a longer lifetime. Drawbacks may be high costs and biological hazards.

4.1.1 Problem Description

The net cages are subject to a harsh environment and may fail, resulting in fish escaping the farm. In addition to loosing profit, unleashing the farmed fish among the wild fish are endangering the diversity of the species [81]. The Norwegian Ministry of Fisheries and Coastal Affairs (Fiskeri- og kystdepartementet) are urging for a solution, but any new material proposed to replace the twine must be certified according to government regulations before use.

Norwegian Standard NS 9415, *Floating fish farming installations – design, dimensioning, construction, installation and operational requirements* places strict technical requirements on fish farming installations [82]. It includes minimum twine tensile breaking strength for various designs and requires that at least 65 % of the strength is left after 24 months of operation. The twine should have higher elasticity than the ropes and a high elongation-at-break percentage is desired to take up energy from impacts and creep. Also, the mesh and rope should not shrink such that forces are transferred from rope to mesh. A low weight is preferred to reduce the strain on the floating collar and ease installation.

The net cage must have a design working life of at least 36 months [82]. Throughout the lifetime, the equipment will be subject to constant fatigue from waves and current in addition to wear from temperature changes, corrosion, UV radiation and maintenance activities. The materials used in the fish farm may not impose the risk of harming the fish, its surroundings or the facility. Additionally, the fish may not under any circumstance bring any toxic agents to its consumer. The net cage should also have a high permeability, meaning water should be able to flow freely through to provide enough oxygen to the fish.

4.1.2 Current Solutions

The established material for the twine is nylon. It fulfills the government requirements, but several incidents of net rupture have called for stronger materials [83]. Mørenot Aquaculture AS has chosen Dyneema as the best replacement for nylon and is currently testing its performance in net cages [84]. To assess CNT yarn, a thorough search for alternative fibers and their properties was performed. The Dutch fiber company Eurofibers [85], a supplier of high performance fibers from leading brands such as Dyneema and Kevlar, was contacted to ask for test results. Their in-house test results was supplemented by data from MatWeb and some vendors, and listed in Table 4.1.

For direct comparison, properties of CNT yarn were included in the same table. Extensive search in scientific journals found properties of 24 CNT yarns spun from CNT arrays and are listed in Table B.1 in Appendix B. The mean and median properties was calculated for the CNT yarn and compared with the commercial fibers in Table 4.1. Because some extreme values are shifting the mean giving a high standard deviation, the median is considered the most reliable. The particularly good result by the reputable Prof. Zhang and his team was included to

show how good the properties may become (CNT yarn Zhang) [86]. In addition, Nanocomp Technologies, an American company already selling CNT yarn was contacted and asked for test results (CNT yarn N.Comp.) [56]. Note that tests are performed in different setups and environments creating some room for error.

TABLE 4.1: Mechanical properties of commercial high performance fibers including CNT yarn.

Brand name	Density [g/cm^3]	E-Modul [GPa]	Tens. strength [MPa]	Tenacity [N/Tex]	Elong. at break [%]	Ref.
Dyneema SK78/75	0,97	121	3 600	3,70	3,5	[85]
Dyneema SK65/62/60	0,97	83	2 850	2,95	3,5	[85]
Dyneema SK25	0,97	52	2 200	2,20	3,5	[85]
Diolen	1,38	N/A	1 049	0,76	12,3	[85]
Twaron	1,39	N/A	2 724	1,96	3,1	[85]
Technora	1,39	70	3 000	2,23	4,4	[24]
Vectran UM	1,4	103	3 000	2,14	2,8	[87]
Zylon HM	1,56	280	5 800	3,71	2,5	[24]
Kevlar 29	1,44	71	2 920	2,03	3,6	[88]
Kevlar 49	1,44	112	3 000	2,08	2,4	[88]
Kavlar 149	1,47	179	3 450	2,35	N/A	[24]
Nylon 6	1,14	N/A	583	0,51	7,8	[24]
Nylon 66	1,22	N/A	507	0,42	8,3	[24]
Spectra	0,97	172	3 000	3,09	N/A	[24]
CNT yarn mean	0,66	101	922	3,43	4,7	Tab. B.1
CNT yarn median	0,68	65	625	1,72	2,4	Tab. B.1
CNT yarn Zhang	0,20	182	2 325	11,74	9,0	[86]
CNT yarn N.Comp.	0,75	N/A	900	1,20	17,5	[56]

4.1.3 Device Design

The business idea is to replace the twine, not modify the design of the net cage. Therefore, only a new twine diameter will be calculated here using the cage in Fig. 4.3 as model. According to Table 8 and 9 in NS 9415, the model is placed in dimension grade VII and should hold a minimum weight of 136 kg [82]. The required CNT twine thickness is calculated using basic mechanics as seen in Eq. 4.1. The strength of commercial CNT yarn from Nanocomp Tech. from Table 4.1 is used in this assessment.

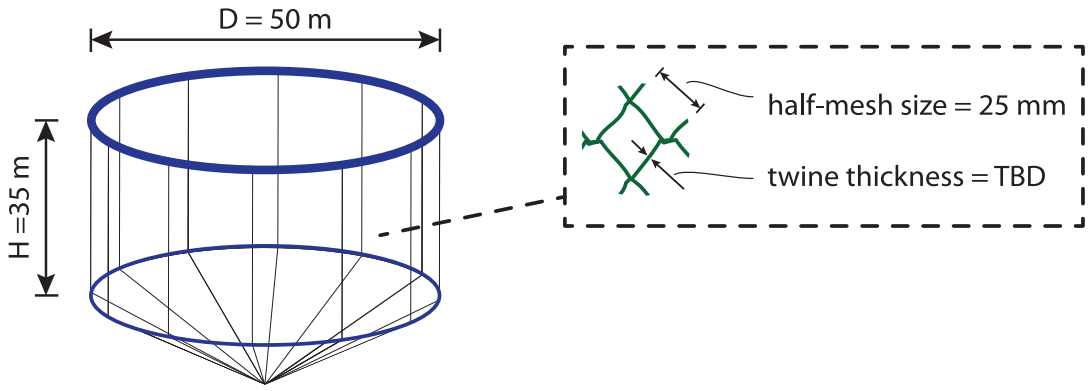


FIGURE 4.3: Size of typical net cage. Twine diameter is to be determined.

$$\sigma_{UTS} = F/A = \frac{m \cdot g}{\pi \cdot D_{min}^2/4} \tag{4.1}$$

$$D_{min} = \sqrt{\frac{4 \cdot m \cdot g}{\pi \cdot \sigma_{UTS}}} \tag{4.2}$$

$$= \sqrt{\frac{4 \cdot 136 \text{ kg} \cdot 9,81 \text{ m/s}^2}{\pi \cdot 900 \text{ MPa}}} = 1,4 \text{ mm} \tag{4.3}$$

To fulfill the government requirement, the CNT twine diameter, calculated by Eq. 4.3, should be at least 1,4 mm. Corresponding calculations for nylon 6 and Dyneema SK60 give 1,7 mm and 0,8 mm respectively.

4.1.4 Discussion

CNT yarn seems to satisfy the government regulations on mechanical properties. It is stronger than nylon, hence requiring lower twine diameter. The toughness of CNT yarn is assumed high due to the large number of nanotube interfaces that can absorb energy by slipping. The yarn has a high elasticity and fulfills the strain requirement. Furthermore, the density is low, making the cage light. The high stability reported in section 2.2.4 suggest long lifetime and little fouling. However, there is a lack of reports on CNT yarn behavior when submerged in water. There is a chance the yarn will swell and loose its strength.

Dyneema is probably the greatest rival to CNT yarn. It is currently much stronger, is well tested in maritime environments and is probably cheaper. Nonetheless, the chemical stability and high toughness of CNTs are in favor of CNT yarn.

The main problem of using CNT yarn in net cages is the health risk. If CNTs are used, the release of CNTs in the water is inevitable. The fish as well as other sea creatures may inhale CNTs and pass them on to its consumer, eventually ending up at the dinner table. It is a risk not worth taking and is destroying the business idea. As long as CNTs are considered toxic, it should not be used in agriculture of any kind.

4.1.5 Further Work

The issue of toxicity and environmental impact of CNTs should be tested thoroughly before continuing this concept. However, using CNT yarn in other maritime industries is not out of the question. A study on CNT yarn behavior in aqueous solution over time should therefore be performed. Because cost is always an issue in comparing materials, a cost analysis of CNT yarn would be helpful.

4.2 Oil Drier with CNT Membrane

Water contamination is a problem in hydraulic and lubricating systems [89]. Up to the saturation point, the water is dissolved in the oil. Around the saturation point, the water emulsifies by gathering into tiny globules. Once the emulsified water accumulates, they form an inclusion of free water. The water may initially be dissolved in the oil when the system is filled. Because the saturation point is lower at low temperatures, the water may condense to free water during operation at reduced temperature. Other sources of water include leakage through seals, gaskets and faulty components. Figure 4.4 show the components of a typical hydraulic system.

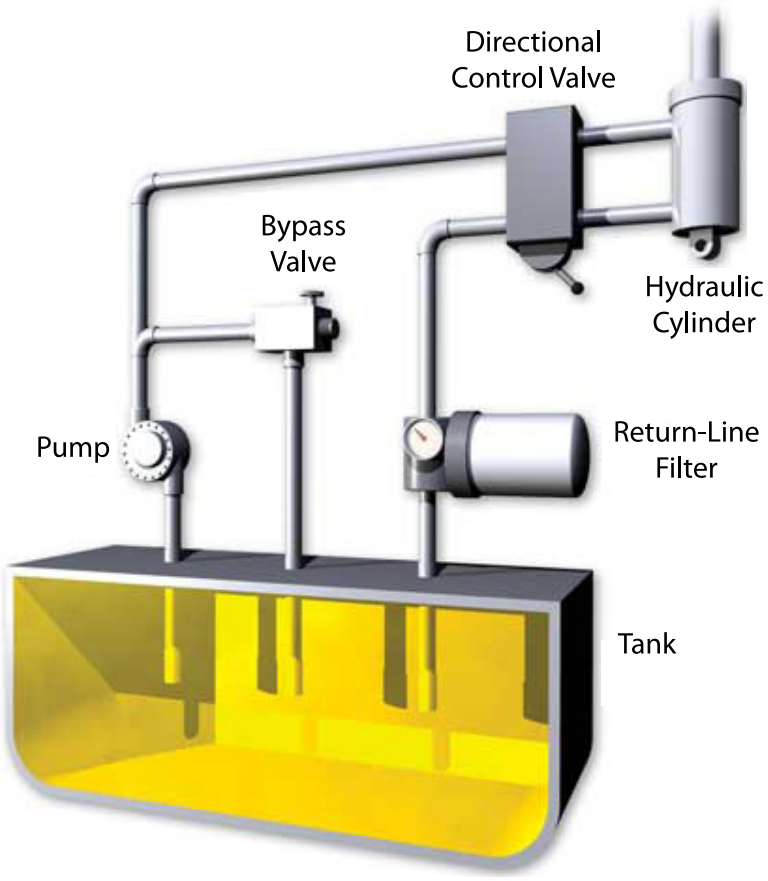


FIGURE 4.4: Illustration of a typical hydraulic system [90].

4.2.1 Problem Description

First of all, water facilitates corrosion. In addition to uniform corrosion on sites of free water, the fluid motion may give erosion-corrosion rubbing away material [91]. If small cracks develop, water may penetrate and cause pitting and hydrogen embrittlement [89]. In valves and pumps, the oil may get a pressure drop vaporizing emulsified water causing cavitation. In cold environments, the water may freeze into damaging ice crystals and in warm environments, the water may be living grounds for oil-eating microorganisms. Furthermore, water reduces the quality of the oil by decreasing lubricity and increasing degradation.

The operating function of a hydraulic or lubricating system intensifies the importance of oil drying. Hydraulic systems are often used to operate large valves and gates in remote systems making the operator very dependent on it. Furthermore, a failure in a lubricating system on a large machine, as seen in Fig. 4.5, may be catastrophic.

FIGURE 4.5: Photograph of roller bearing subject to water damage [92].

4.2.2 Current Solutions

Current solutions for removing water from oil tackle the water states differently. The simplest approach is draining the oil reservoir of both air and free water by turning valves in the top and in the bottom [89]. Air rises to the top and water sinks to the bottom. Secondly, centrifuges may be installed in the pipeline to remove both free water and some emulsified water by exploiting the different densities, although this requires high installation and maintenance costs. The third solution is to use a filter to collect and fuse emulsified water into free water

for draining, called a coalescer. This approach does not work for all types of oils and may be hindered by clogging. If the amount of free water is small, an absorbing filter may be used to remove free and emulsified water. Obviously, such a filter must frequently be replaced. If the dissolved water must be removed as well, vacuum dehydration purifiers are used. Vacuum makes the dissolved water boil and the steam is removed through valves. The latter removes all states of water, but the investment and maintenance are expensive.

4.2.3 Device Design

The device proposed here is fundamentally different from the previous techniques. It is composed of a filter that blocks instead of absorbing the water. It should require less maintenance and have a longer lifetime. The working principle and design will be explained.

Working Principle

As recently shown by Shi et al., a sheet of entangled CNTs may separate emulsified oil/water mixtures [59]. Their membrane, seen in Fig. 4.6, was able to purify a water contaminated solution of surfactant-stabilized oil (Toluene) from 99,00 wt% to 99,97 wt% (350 ppm) at a flux of $3\,090\,\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$. Because of the contact angle of water droplets, measured to 94°, the droplet keeps its shape and rests on top of the membrane. The same test on oil droplets resulted in a contact angle of nearly 0°, i.e. the oil spread out. When the oil/water mixture is placed on top of the membrane, the oil suffuses and penetrates whereas the water congregates on top. Key parameters of success are membrane pore size controlled by the membrane thickness and the pressure difference through the membrane.

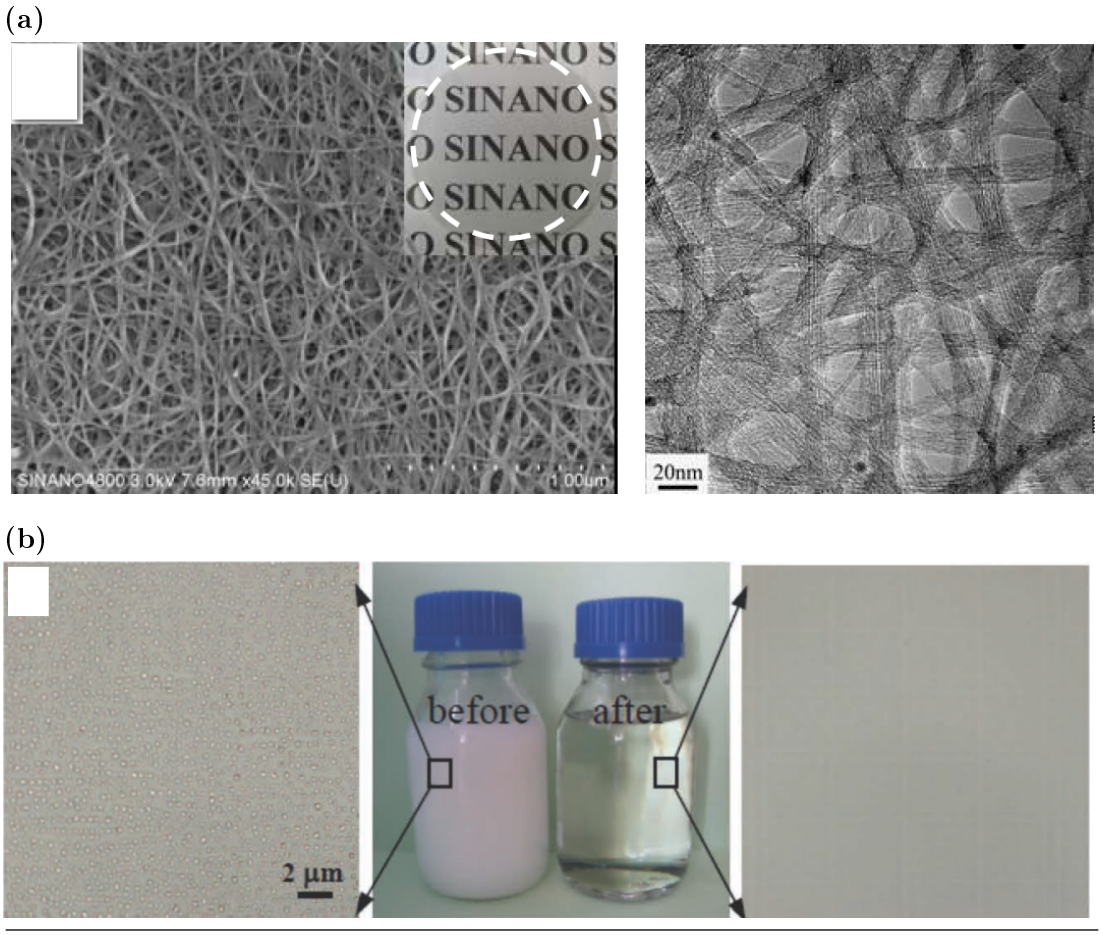


FIGURE 4.6: Figures from Shi et al. [59]. **(a)** Fig. S1,D. Left: SEM image of 70±5 nm thick CNT membrane, inset: optical microscopy of transparent membrane on top of a printed document. Right: TEM image of CNTs in membrane **(b)** Fig. 3,C. Optical microscopy of solutions before (left) and after (right) filtration of Toluene with water droplet size 270±50 nm. Middle: Photograph of the respective solutions.

Design

A simple design turning the research membrane into a commercial product has been developed. A steel cone with vertical openings as seen in Fig 4.7a will work as framework and support the membrane. The membrane (Fig. 4.7b) should consist of CNTs and have a predetermined pore size and thickness according to oil properties. The membrane can either be made by filtering a CNT solution and placed on the cone as in Fig. 4.8a, or it can be made by pulling a fabric from a CNT array and winded onto the cone as in Fig. 4.8b.

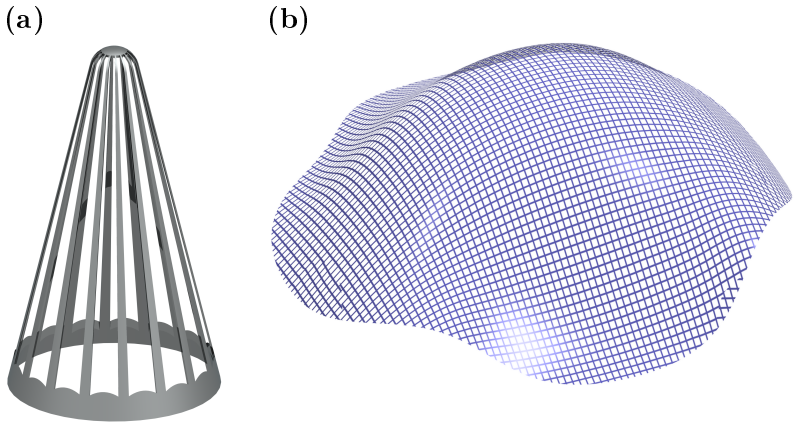


FIGURE 4.7: Main components of CNT filter. **(a)** Steel cone with vertical openings. **(b)** Flexible CNT membrane.

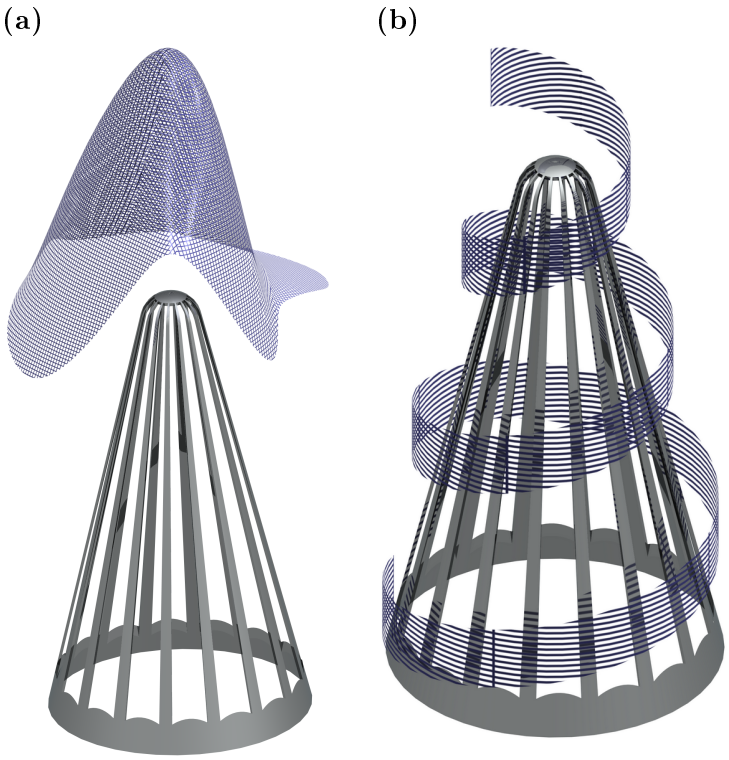


FIGURE 4.8: Illustrations of ways to put the CNT membrane onto the cone. **(a)** Make the membrane by filtering a CNT solution and place it on the cone. **(b)** Pull a CNT fabric from a CNT array and wind it directly onto the cone.

The filter unit, seen in Fig. 4.9a, is 250 mm high and has a bottom diameter of 75 mm. The effective filter area of the device (the area of the openings) is calculated to be approximately 60 cm^2. Using the measured flux (3 090 $L\,m^{-2}\,h^{-1}\,bar^{-1}$)

of the Toluene solution from Shi et al. and a pressure difference of 0,5 bar, the filter flow rate is calculated to 0,15 L/min by Eg. 4.5 [59]. The filter unit will let oil pass through in the center and guide the water to the side as seen in Fig. 4.9b.

$$Q = \text{Flux} \cdot \text{Area} \cdot \text{Pressure} \tag{4.4}$$

$$= 3090 \frac{L}{m^2 \cdot h \cdot bar} \frac{1h}{60min} \cdot 60 \cdot 10^{-2} m^2 \cdot 0,5bar = 9,12L/h = 0,15L/min \tag{4.5}$$

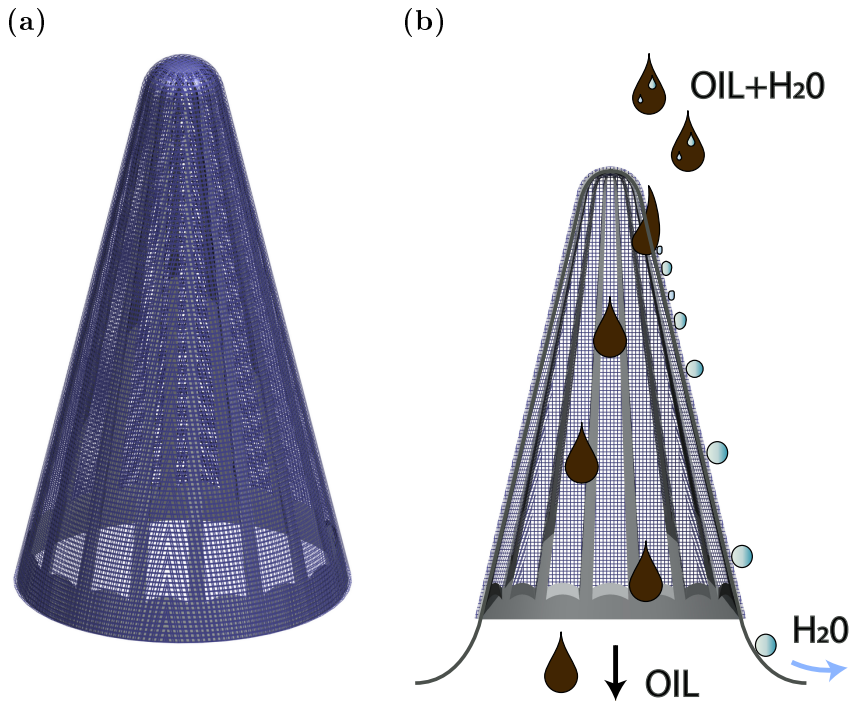


FIGURE 4.9: **(a)** Illustration of complete CNT filter unit. **(b)** Cross section image of filter unit showing how water is blocked and guided to the side.

A simple assembly include a filter, some pipes and a spiral case as seen in Fig. 4.10. The water/oil mixture enters at the top and runs through the conical filter. Water is collected around the bottom of the cone and collected in the spiral case before guided out to the side. Only the oil penetrates the membrane and passes through.

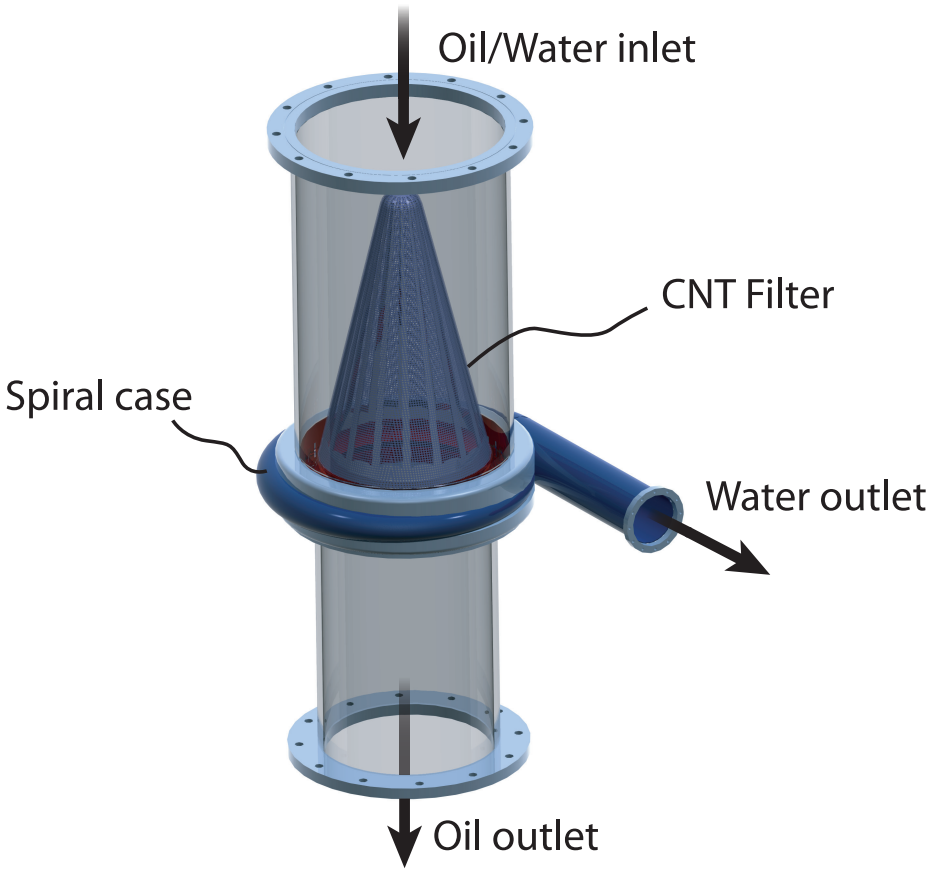


FIGURE 4.10: Illustration of oil drier with CNT membrane assembly.

4.2.4 Discussion

This device is developed following a series of articles presenting the idea of oil/water separation by CNT membranes [58, 59, 93]. It is expected that others have the same business idea and would like to commercialize it. In fact, patents applications are already pending for CNT filters [94]. If the device proposed here is to be continued, the examination of patent applications and possible filing of own patent should be commenced.

The specific filter designed here was calculated to filter Toluene at 0,15 L/min. Even though oil driers are needed in all sizes, the filter should probably filter at least 1 L/min to compete with other techniques [95]. The simplest solution would be to increase the cone height, in turn increasing the filter area. Furthermore, Toluene is a low viscosity oil mainly used as solvent. Tests on thicker commercial oils more common in hydraulic and lubricating systems are needed.

To handle the pressure difference through the membrane, the mechanical strength of the carbon nanotubes are needed. It is not clear which of the membrane fabrication techniques suggested here, filtering dispersed CNTs on a grid or pulling a fabric from a CNT array, are optimal.

Issues of health risk and cost are well handled in this device. The CNTs are contained in a closed conduit system with low risk of leakage. The amount of CNTs in a filter is considered low, hence the cost is held low. Fabrication of a prototype should not require any large investments.

4.2.5 Further Work

A proof that the CNT membrane works with hydraulic and lubricating oils is necessary. Membranes of different pore sizes should be acquired and tested with various oils with different viscosities, droplet sizes and water fractions. In addition, a more thorough study of patents and patent applications on CNT filters is needed.

Chapter 5

Fabrication

FIGURE 5.1: Picture of the author operating the PECVD at NTNU Nanolab.

The value of a concept boosts once a successful prototype has been made. A critical part of making the proposed devices, net cage and oil drier, is the fabrication of CNTs and making of the yarn or fabric. The following chapter will cover the growing of VACNTs at NTNU Nanolab. The entire procedure will be elucidated including equipment settings, results and discussion.

5.1 Introduction to Growth of CNTs

Before attempting to grow CNTs, a thorough understanding of the CNT characteristics and fabrication method is essential. Due to previous experience with growing of VACNTs, it is decided to make the CNT membrane and yarn using the pulling technique described in section 2.3.4.

5.1.1 Target Characteristics of CNTs

The success in pulling either yarn or fabric from a CNT array is highly dependent on the characteristics of the CNT array. The following section will determine the target characteristics of the CNT array for CNT yarn fabrication. The targets are expected to hold for both yarn and fabric.

Several research groups have tried to come up with criteria for VACNTs for yarn pulling. Lee et al. were only able to make yarn with CNT length in the range of 180 – 1 500 µm [96], whereas Kutnetsov et al. concluded that the CNT length must be within 50 – 800 µm [97]. However, the collection of CNT yarn characteristics seen in Table 5.1 prove them both wrong. The length issue is more likely related to the waviness and entanglement occurring at long growth times, not the length itself. For the pulling technique to be effective, the tubes need to separate easily in the centers and join together in the ends as illustrated by Fig. 5.2 [98]. Therefore, the tubes should be straight and pure in the centers and dense and entangled in the ends. If the density is too high, the stress among the tubes during growth could result in some tubes detaching from the substrate [96]. If this happens, the density at the bottom gets reduced and yarn pulling difficult.

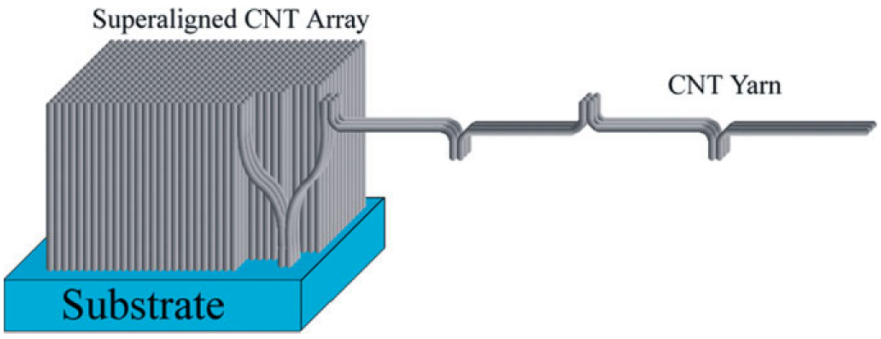


FIGURE 5.2: Illustration of how entanglement in top and bottom of CNT array connect the individual CNTs while pulling a yarn [98].

TABLE 5.1: CNT characteristics from successful CNT yarn pulling. More details found in Appendix B. Abbreviations explained in the front matter.

Diameter [nm]	Length [µm]	Walls	Growth method	Ref.
10	300	MWCNT	CVD	Aliev et al. 2007 [99]
N/A	300	MWCNT	CVD	Atkinson et al. 2007 [100]
N/A	550	MWCNT	CVD	Atkinson et al. 2007 [100]
15	500	MWCNT	WACVD	Jakubinek et al. 2012 [101]
10,5	5 000	MWCNT	CVD	Jayasinghe et al. 2011 [102]
15	450	MWCNT	CVD	Kuznetsov et al. 2011 [97]
10	425	MWCNT	N/A	Liu et al. 2010 [103]
10	235	MWCNT	N/A	Liu et al. 2010 [104]
N/A	170	MWCNT	CVD	Nakayama 2008 [105]
8	350	MWCNT	CVD	Randeniya et al. 2010 [106]
5,5	720	DWCNT	PECVD	Ryu et al. 2011 [107]
8	350	MWCNT	CVD	Tran et al. 2009 [108]
8	350	MWCNT	CVD	Tran et al. 2011 [109]
11,5	100	MWCNT	CVD	Zhang et al. 2004 [54]
7	1 000	DWCNT	CVD	Zhang et al. 2007 [86]
10	650	MWCNT	CVD	Zhang et al. 2007 [110]
10	1 000	MWCNT	WACVD	Zhang et al. 2008 [111]

Zhang et al. performed strength measurements on CNT yarn made of CNTs with different lengths grown by chemical vapor deposition (CVD) [110]. They discovered the fiber strength increases as the CNT length increases as seen in Fig. 5.3, hence longer tubes are preferred for load bearing applications. Furthermore, longer tubes are expected to be of less health risk as they can be considered as articles, not particles [56].

From the previous reports of CNT yarn fabrication, a requirement specification for the CNT array is made. These requirements, seen in Fig. 5.4, will work as guide when the parameters of the fabrication equipment are determined and when evaluating the fabrication results.

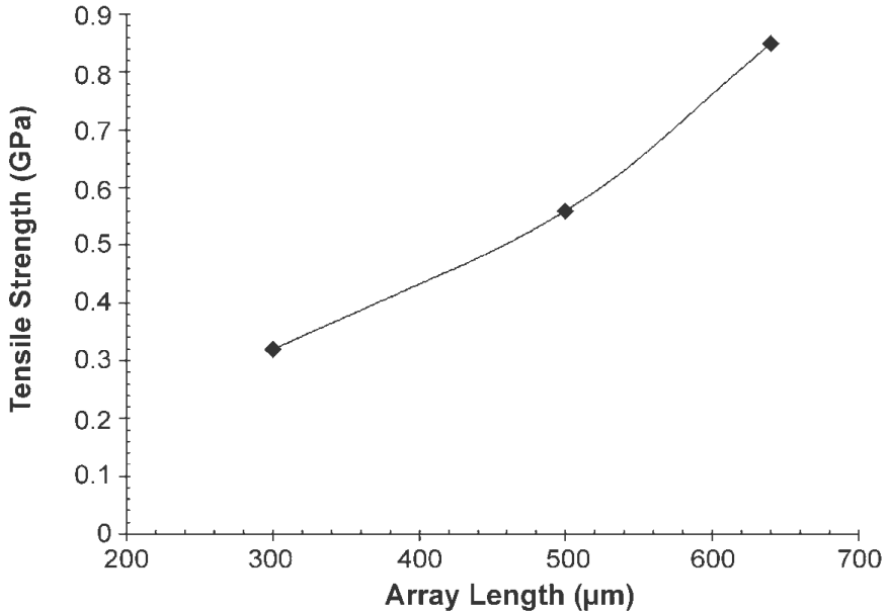


FIGURE 5.3: Tensile strength of CNT yarn made by CNT array of three different tube lengths. Longer tubes yield higher tensile strength [110]

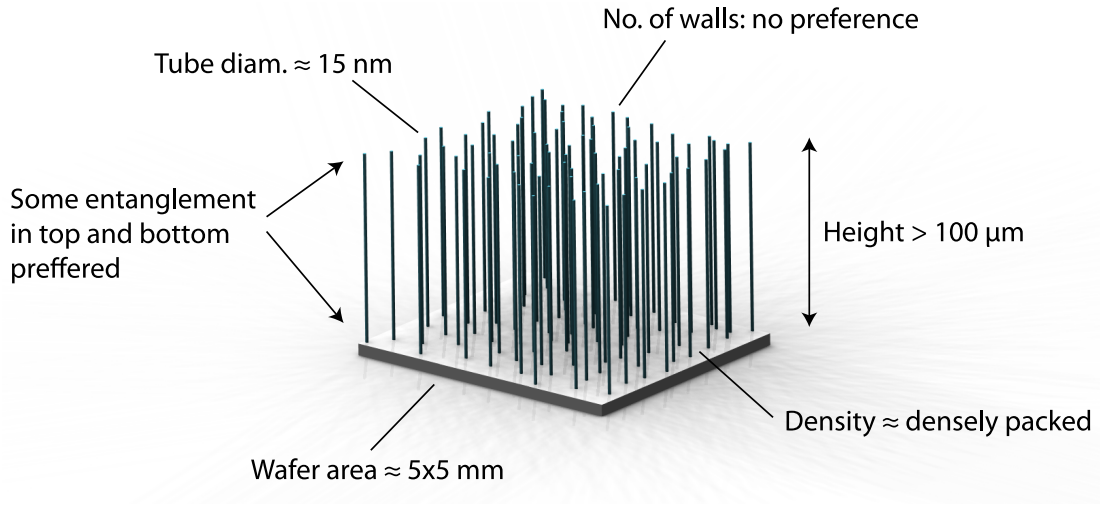


FIGURE 5.4: Requirement specification for the VACNTs. A height higher than 100 μm is of particular importance.

5.1.2 Growth Mechanisms of PECVD

The CNTs will be grown by plasma-enhanced chemical vapor deposition (PECVD). PECVD has a large amount of parameters to control and their correlations are not fully understood. The technique involves mixing a carbonaceous gas and plasma

such that carbon atoms are released and deposited into a tube [112]. The growth mechanism in a PECVD as the one in Fig. 5.5 is shortly reviewed.

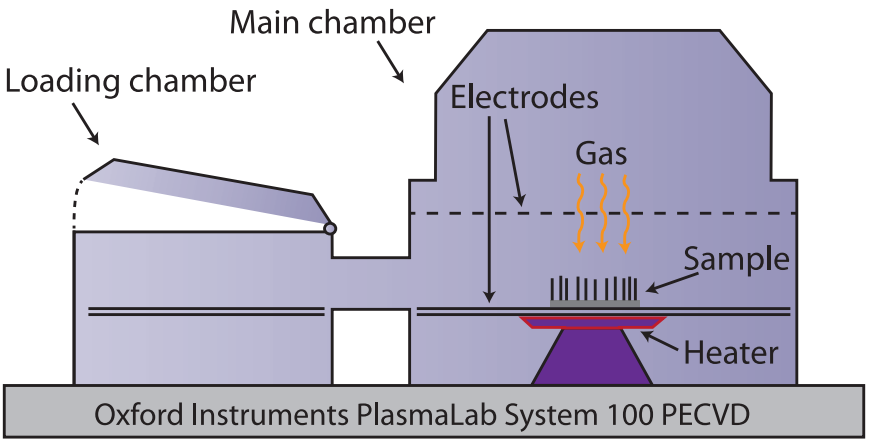


FIGURE 5.5: Schematic of the PECVD located at NTNU Nanolab. The sample is inserted in the loading chamber and a loading arm moves the sample into the main chamber. The top electrode is a disk with holes to let the process gasses penetrate. The sample rests on top of a heater/electrode.

A wafer coated with a layer of catalyst, here iron, is inserted into a chamber at high vacuum and high temperature [113]. The sample is heat treated such that the catalyst recrystallizes to form spherical catalyst particles of a specific size. A gas, usually ammonia, nitrogen or hydrogen is added to control the process called pretreatment. Step two is the growth of CNTs where a gas containing carbon enters the chamber, supplemented by control gasses such as ammonia, nitrous oxide and/or hydrogen. To decompose the gas and release the carbon atoms, a plasma ignited by an alternating radio frequency voltage, excite the gas molecules. The released atoms diffuse to the catalyst particle and deposit on the edges creating a ring of carbon as seen in Fig. 5.6. Maintaining this process makes the carbon grow into a tube with the catalyst resting on top, called top growth. After a preset growth time, the chamber is purged and pumped to remove gases, cooled down and the sample is extracted.

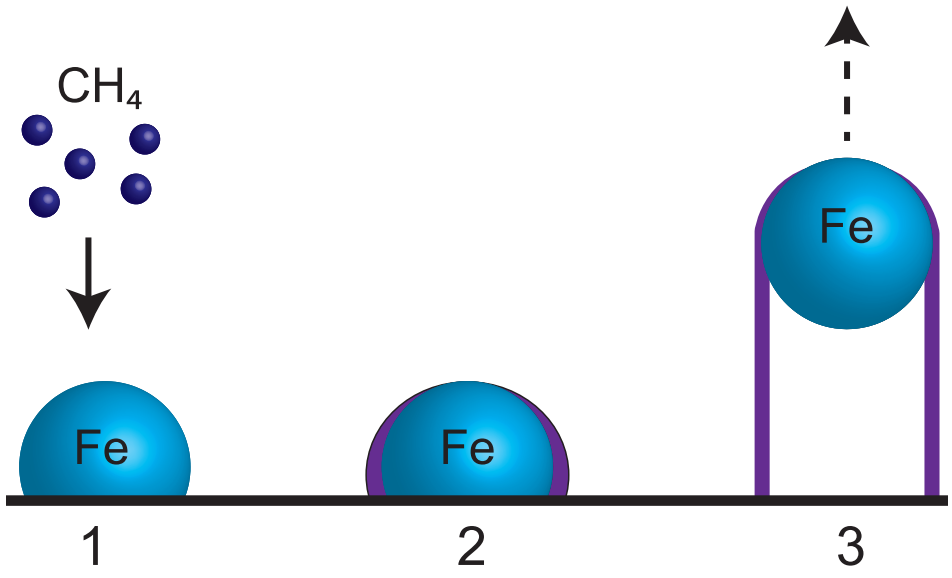


FIGURE 5.6: Schematic of VACNT top growth. 1. Carbonaceous gas is introduced. 2. The carbon atoms decompose and attach to the catalyst. 3. The carbon forms a ring at the underside of the particle. Frequent addition of carbon atoms makes the catalyst particle rise, growing a VACNT.

The van der Waals forces make the tubes repel each other aligning them vertically. In addition, the plasma assists alignment by introducing a strong vertical voltage potential [13]. The problem with using plasma is the risk of etching. If the effect is too high or the growth step too long, the plasma may etch away the catalyst and tubes completely [113].

5.1.3 Initial Equipment Parameters

The master's thesis by M.Sc. Karl Erik Nordheim lay the foundation on growing CNTs at NTNU Nanolab [50]. Of Nordheim's 226 different recipes, 38 of them yielded VACNTs including recipe E47 seen in Table 5.2. His data will be used to derive the initial parameters for CNT yarn fabrication.

TABLE 5.2: Successful CNT recipe E47 by Nordheim [50].

Step	Description	Equipment	Parameters
1	Cut sample	Scriber unit	5x5 mm, 250 µm thick Si-wafer
2	Clean sample	Solvent bench	Acetone, Ethanol, DI-Water, N_2
3	Dehydrate sample	Hot plate	180 °C, 2 min
4	Deposit barrier layer	Sputter coater	30 nm Al
5	Oxidize barrier layer	RTP Oven	500 °C, 50 0 sccm O_2, 30 min
6	Deposit catalyst	Sputter coater	1 nm Fe
7	Slow heating	PECVD	300→650 °C, 50 sccm NH_3, 0 mTorr, 30 min
8	Pretreatment	PECVD	650 °C, 50 sccm NH_3, 1 000 mTorr, 30 min
9	VACNT growth	PECVD	650 °C, 50 sccm CH_4, 1 000 mTorr, 100 W, 60 min
10	Slow cooling	PECVD	650→300 °C, 1 200 sccm Ar, 0 mTorr, 120 min

Nordheim had best success with a catalyst layer thickness of 1 nm as seen in Fig. 5.7. The reason is probably that thicker catalyst layers have trouble forming particles in the pretreatment. Furthermore, he tested the use of N_2O instead of NH_3 in step 8. Once he changed the gas to N_2O, the recipe yielded VACNT for catalyst layer thickness 1, 3, 6 and 10 nm (Fig. 5.8).

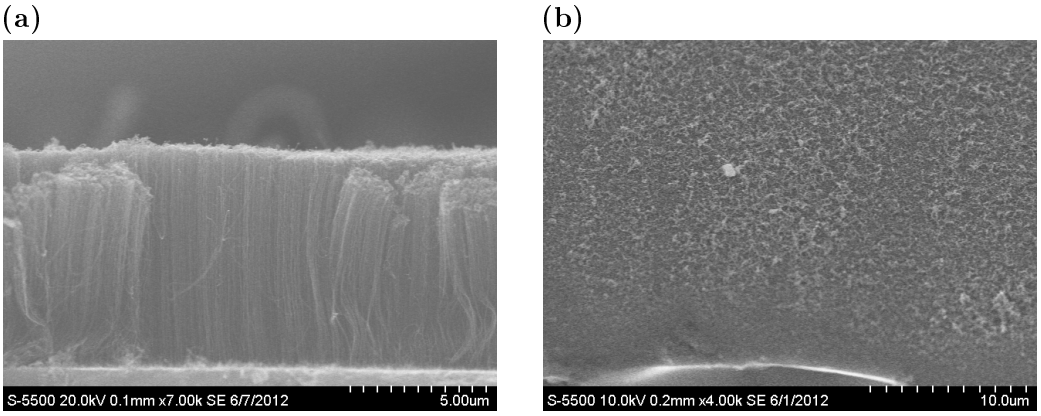


FIGURE 5.7: SEM images showing dependence on catalyst layer thickness [50]. **(a)** Recipe E47, catalyst thickness 1 nm. 90° tilt. VACNT. **(b)** Recipe E48, catalyst thickness 3 nm. 30° tilt. No VACNT.

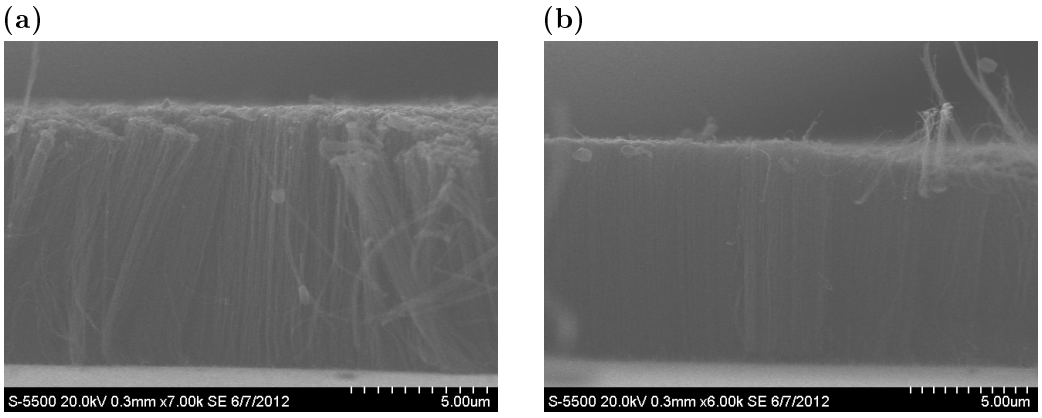


FIGURE 5.8: SEM images showing dependence on pretreatment gas at 90° tilt [50]. **(a)** Recipe E115. Replaced NH_3 with N_2O in pretreatment. Catalyst thickness 1 nm. VACNT. **(b)** Recipe E116. Replaced NH_3 with N_2O in pretreatment. Catalyst thickness 3 nm. VACNT.

The E47 recipe had a heating and cooling cycle (step 7 and 10), but this seemed to inhibit growth. As seen in Fig. 5.9, samples with both 1 nm and 3 nm catalyst thickness was successful when these steps were left out. It also resulted in an increased growth rate for these samples as recipe E167 had a growth rate of 0,48 µm/min, the highest of all recipes.

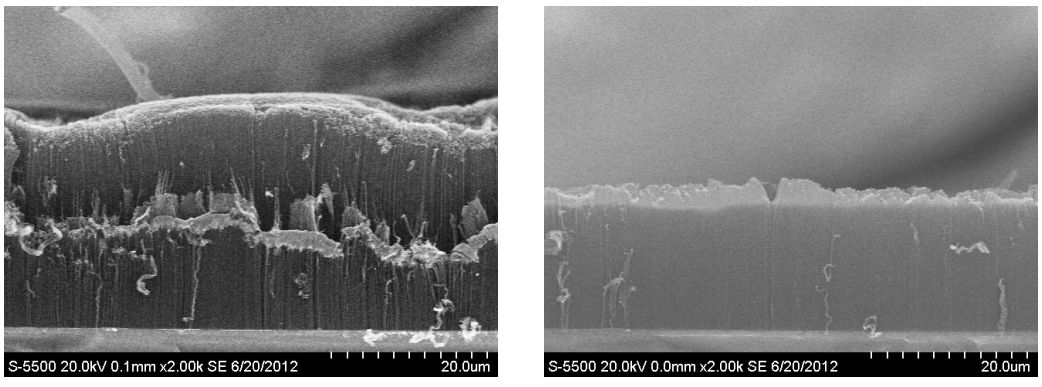


FIGURE 5.9: SEM images showing dependence on heating and cooling cycle at 90° tilt [50]. **(a)** Recipe E167, heating and cooling removed, catalyst thickness 1 nm. VACNT. **(b)** Recipe E168, heating and cooling removed, catalyst thickness 3 nm. VACNT.

5.2 Method

In cooperation with Espen Rogstad, NTNU Nanolab Chief Engineer, growing of CNTs was attempted. The goal was to grow CNTs that fulfill the specifications in Fig. 5.4 with an easily reproducible recipe. The established reference recipe, called R01, will hereby be explained. A more detailed procedure may be found in Appendix C, the equipment is listed in Appendix D and some notes on handling and storage are found in Appendix E.

A small piece measuring 5x5 mm was cut out of a 51 mm (2 inch) diameter, 250 µm thick silicon wafer using an automatic scriber. The piece was cleaned by putting it in a beaker filled with acetone and lowered into an ultrasonic bath for 5 min at 20 °C. The sample was then transferred to a beaker with ethanol to rinse off the acetone. Finally it was sprayed with isopropanol and deionized water, followed by blow drying with nitrogen gas. The sample was dehydrated for 5 min on a hot plate at 185 °C.

To prevent contamination of silicon in the catalyst, a 30 nm aluminum barrier layer was deposited using a water-cooled sputter head in an argon atmosphere. The barrier was further enhanced by oxidation in a rapid thermal processing oven for 30 min at 500 °C with 500 sccm O_2. The 1 nm iron catalyst layer was deposited with the same sputter coater, but without water-cooling. For easier imaging of the samples cross section, a piece of tape was put along one of the sides to prevent growth on a small strip.

The final steps take place in the PECVD pre-set at 650 °C. The sample is loaded into the chamber where the chamber preparation includes purging nitrogen gas for 2 min and pumping to a base pressure of $1,5 \cdot 10^{-5}$ using 22 min. Further thermal pretreatment is done by adding 50 sccm NH_3 at 1 000 mTorr for 30 min, that is 54 min at 650 °C pretreatment in total including chamber preparation time. At last, 50 sccm methane gas at 1 000 mTorr is added to feed the growth with carbon. The growth time is 120 min and a plasma of 100 W is present the whole time. Chamber dispatch includes a pump-purge cycle, pumping to base pressure and lowering the temperature to 435 °C. Every run in the PECVD is logged and the log of recipe R01 is seen in Fig. 5.10.

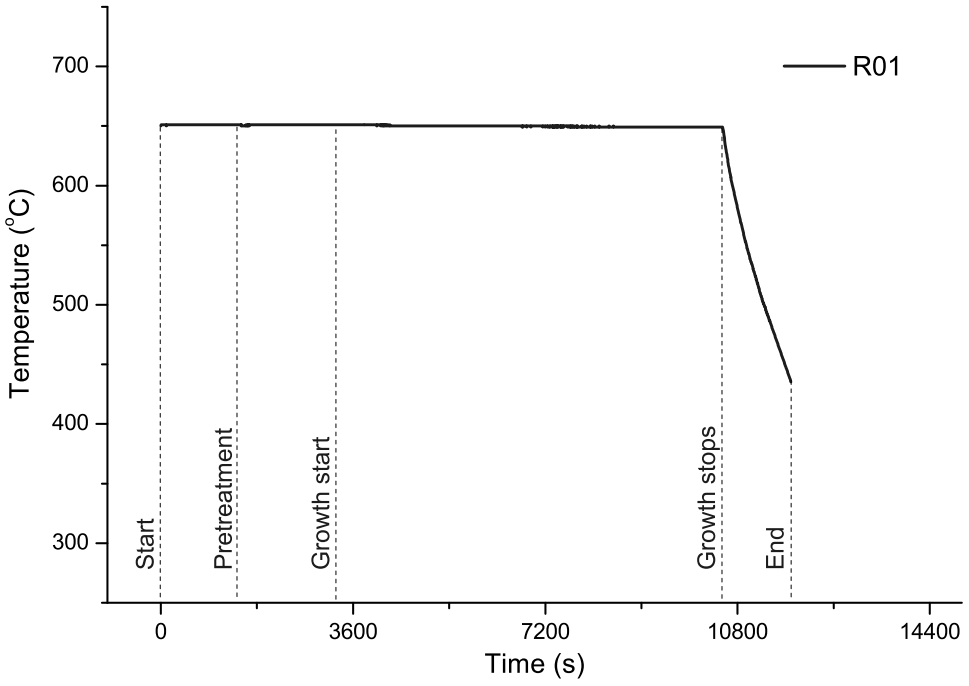


FIGURE 5.10: Graph showing the temperature development through the processing of reference recipe R01 in the PECVD with main steps labeled. During growth, the temperature is stable at 650 °C, but drop to 435 °C during dispatch.

Visual inspection of samples after fabrication was the first assessment of the recipe. The second characterization technique was cross section imaging by optical microscopy. The sample was attached to a SEM stub, mounted on a sample holder and laid on the side in the microscope. The third technique was imaging by scanning electron microscopy (SEM).

With basis in the reference recipe R01, several alternative recipes have been attempted. However, due to process irregularities like equipment failure and shattered samples, some results have been rejected. Table 5.3 present the parameters that have been subject to change in the completed attempts.

TABLE 5.3: Differences between recipes for VACNT growth.

Parameter	R01	R02	R03	R04	R05	R06	R07	R08
Al thickness [nm]	35,0	35,0	30,0	30,0	30,0	30,0	30,0	30,0
Chamber prep. time [min]	24	5	5	101	12	12	15	15
Pretreatment time [min]	30	15	30	45	48	48	30	30
Growth time [min]	120	120	120	60	120	60	60	120
Pretreatment gas	NH_3	NH_3	NH_3	NH_3	NH_3	NH_3	N_2O	N_2O
Enter temp [°C]	650	300	650	650	650	650	650	650
Dispatch temp [°C]	435	419	436	412	422	425	300	300

5.3 Results

When doing visual inspection, all samples had a dim black color as seen in Fig. 5.11.

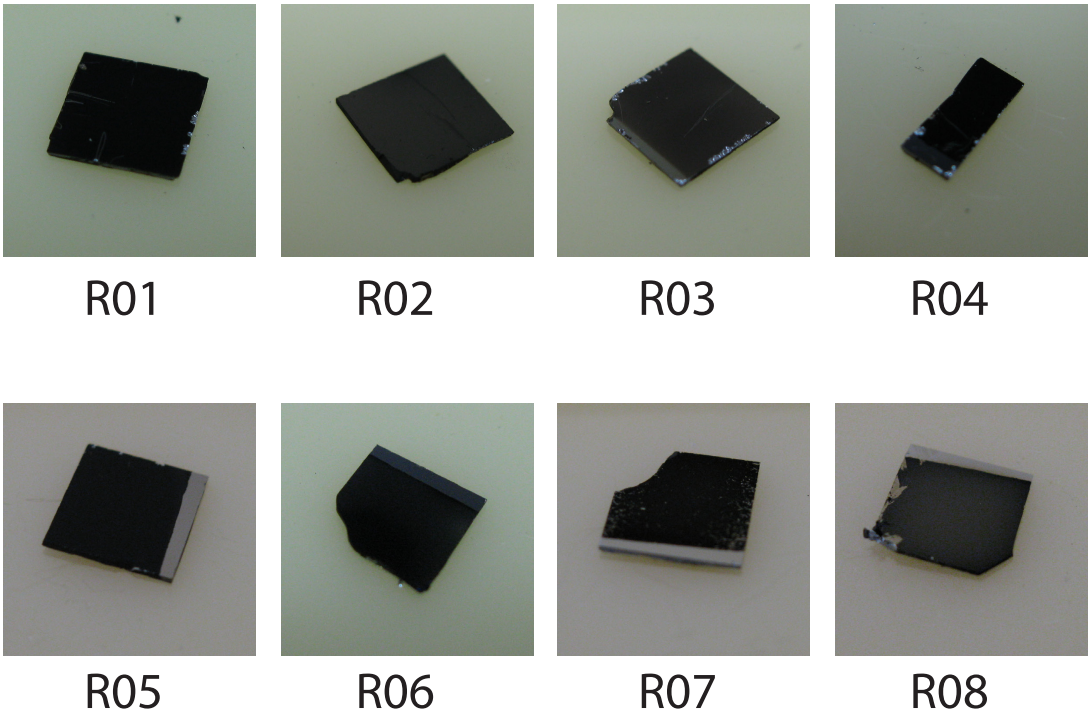
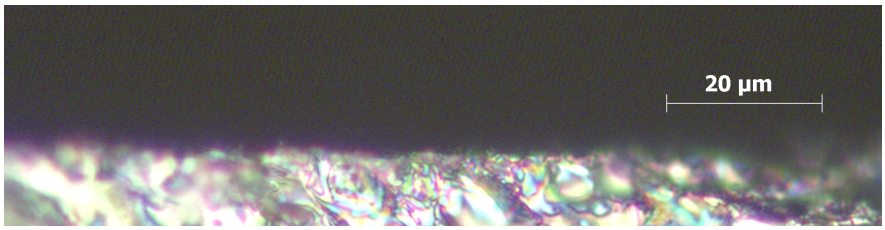


FIGURE 5.11: Photograph of all samples.

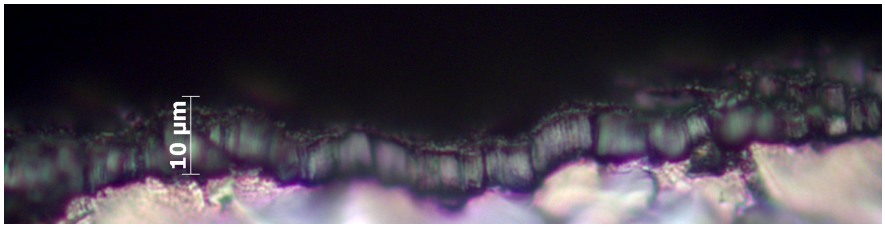
The cross section imaging by optical microscopy was a relatively easy procedure, but the images could only give the height of the deposited layer as seen in Fig. 5.12.

However, some pictures, like Fig. 5.12b, show distinct vertical lines indicating something aligned.

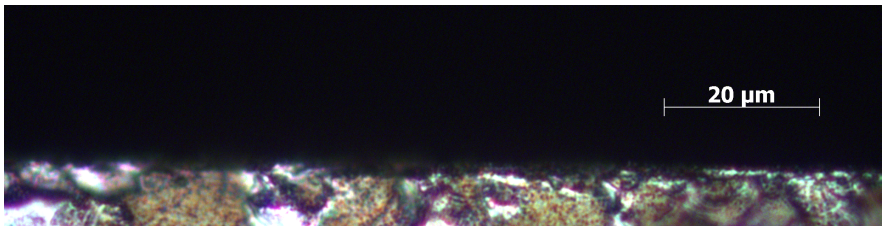
(a)



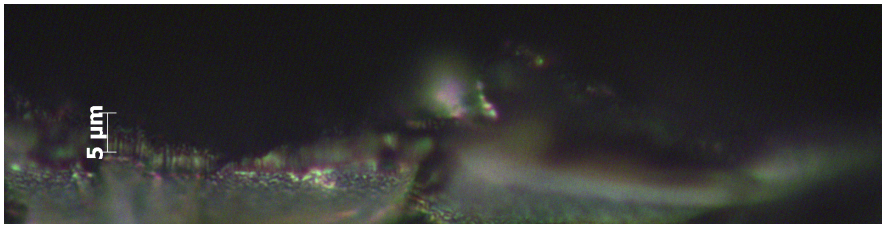
(b)



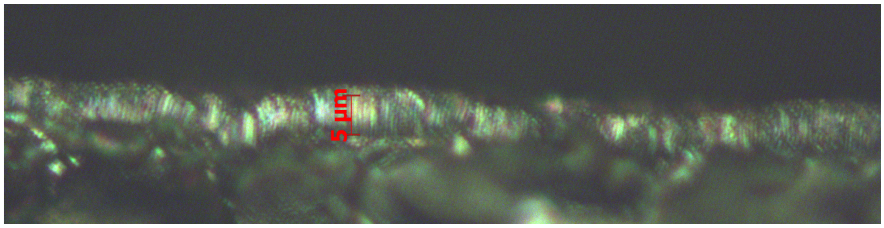
(c)



(d)



(e)



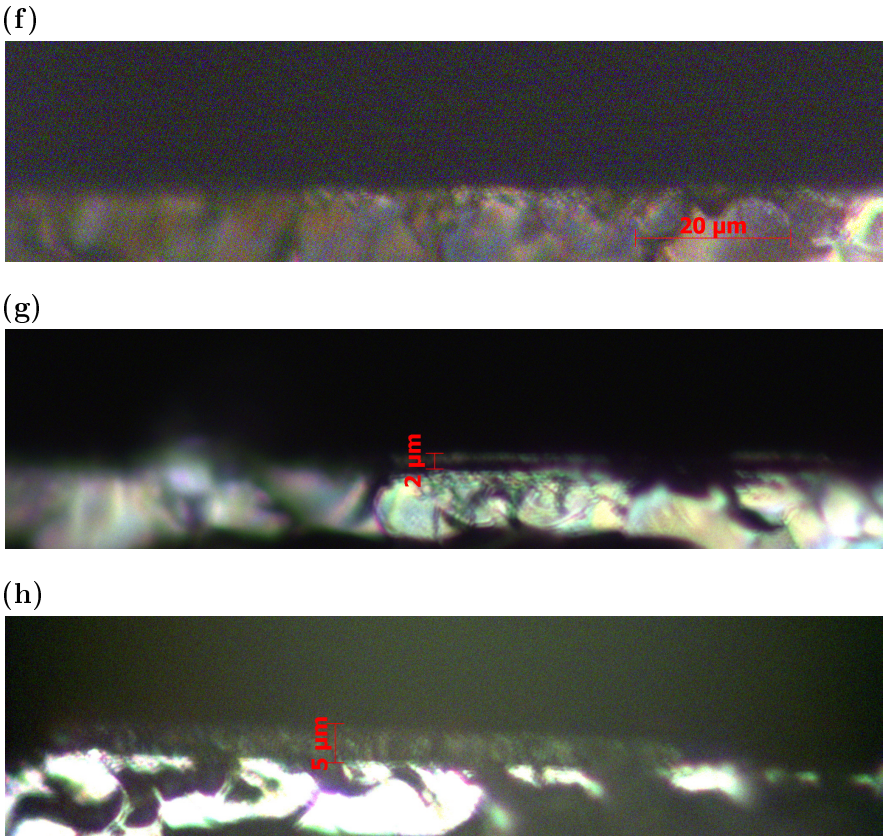


FIGURE 5.12: Digital photography through optical lens of sample's cross section. **(a)** Sample R01. **(b)** Sample R02. **(c)** Sample R03. **(d)** Sample R04. **(e)** Sample R05. **(f)** Sample R06. **(g)** Sample R07. **(h)** Sample R08.

SEM was used to study the samples even closer. At first, imaging was attempted by a TableTop SEM but appeared to be useless due to low resolution. SEM with a FIB installed was then used which proved to be successful with the help of fellow student Marius Vebner. SEM images of 52° tilted samples R01 and R04 may be seen in Fig. 5.13a and 5.13c. The remaining samples were imaged in a Zeiss FE-SEM at a tilt of 30°. SEM of R03 and R06 was omitted due to lack of sign of CNT by optical microscopy.

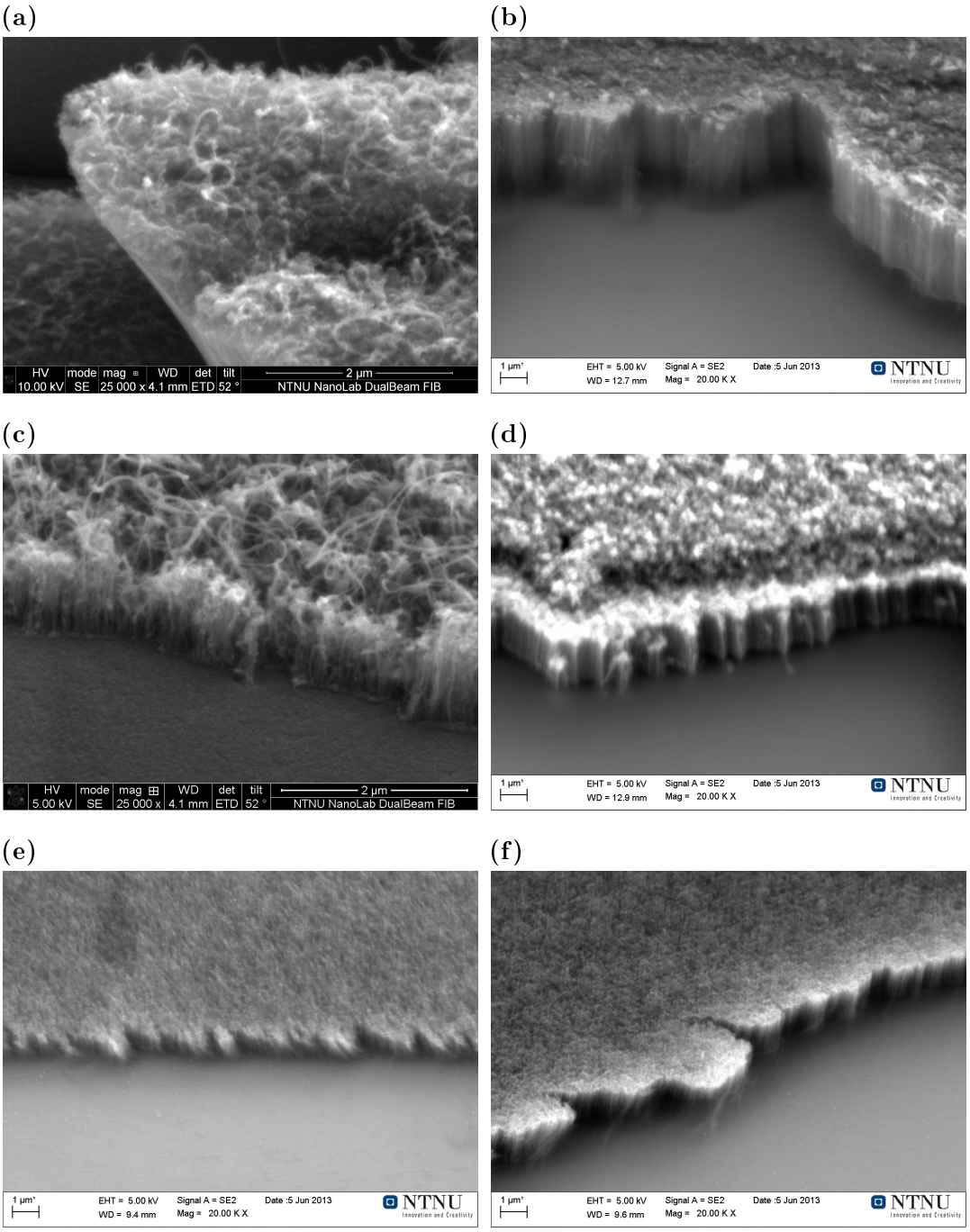


FIGURE 5.13: SEM images of samples from two different electron microscopes. **(a)** Sample R01, tilt 52°. By M. Vebner. **(b)** Sample R02, tilt 30°. **(c)** Sample R04, tilt 52°. By M. Vebner. **(d)** Sample R05, tilt 30°. **(e)** Sample R07, tilt 30°. **(f)** Sample R08, tilt 30°.

The color of the samples and cross section imaging by optical microscope indicated CNTs. SEM images reinforced this assumption. Using basic geometry, the height of each sample was calculated from the tilted images from SEM. Table 5.4

summarize the measured heights from both optical microscopy and SEM as well as own observations from the images.

TABLE 5.4: Measured heights of the deposited layer by optical microscopy (Opt.M.) and SEM. SEM images are used to determine whether CNTs and VACNTs are present.

Parameter	R01	R02	R03	R04	R05	R06	R07	R08
Opt.M. height [µm]	0	8	0	3	6	0	2	5
SEM height [µm]	0	6,6	-	1,1	3,4	-	1,2	2,4
CNT	Yes	Yes	-	Yes	Yes	-	Yes	Yes
VACNT	No	Yes	-	No	Yes	-	Yes	Yes

5.4 Discussion

During the first attempts to grow CNTs (R01 and R02), the Al and Fe layer was deposited on several samples at a time and stored until their time in the PECVD. This was soon altered such that the Fe layer was deposited just before the sample was put into the PECVD to make sure the catalyst did not corrode. However, sample R02 had five days between deposit of Fe and PECVD, hence the timing is not that crucial. Also, the change in thickness of the Al barrier layer is probably not of importance.

Despite the PECVD's simple user interface it introduced some issues. Perhaps the greatest issue was the irregularity in the time it took to pump to base pressure in chamber preparation. As seen in Table 5.3, recipe R04 used 99 min to pump to base pressure and 2 min to purge N_2 (101 min in total). The pump to base step in the other attempts was either much quicker or restricted to a limited amount of time. One occurrence of failing to raise the temperature to 650 °C was experienced, but was fixed by restarting the power source. Furthermore, one attempt failed due to the loading arm being uneven.

By the look of the SEM image of recipe R04 (Fig. 5.13c), it seems as the CNTs have bowed down. A possible explanation is the thermal shock from 412 °C to 23 °C it experienced when the sample was taken out of the chamber. Recipe R07 and R08 was therefore altered by lowering the dispatch temperature to 300 °C. However, no direct correlation on dispatch temperature could be made on such few experiments.

Sample R07 and R08 were pretreated with N_2O instead of NH_3. It is observed that the doubling of growth time gave a doubling of the VACNT height. Whether the growth is in fact linear is unsure.

The purpose of the characterization was to prove the existence of VACNTs, determine the density, height and entanglement or, if unsuccessful, indicate what might have gone wrong. The optical microscope was able to indicate CNTs in a quick and inexpensive way, but SEM was the only technique capable of showing their cylindrical structure. However, SEM could not clarify if the structures were carbon nanotubes or carbon nanofibers (without a hollow core). For such assessment, Transmission Electron Microscopy (TEM) should be used.

Height measurements taken in the optical microscope were all higher than the ones taken by SEM. Whether this is a natural scattering or an effect of the wavelength of light being close to the height of the tubes is not clear. Nevertheless, the SEM measurements are more accurate. The maximum height achieved was 6,6 µm. However, the height requirement in Fig. 5.4 was set to 100 µm. They are therefore not suitable for yarn or fabric pulling.

By comparing the equipment limitations of the PECVD with parameters of successful growth of VACNT in literature it is evident that the unit is not optimal for such experiments illustrated by Fig. 5.14. The upper and lower values of the boxes are values from successful VACNT fabrication in literature with the blue line as the most popular value. The green values are the equipment limitations and the red is the settings of recipe R02. The PECVD can only provide a low gas pressure and have trouble reaching high temperatures. In addition, the installed gases are less favored for CNT growth than for instance C_2H_2.

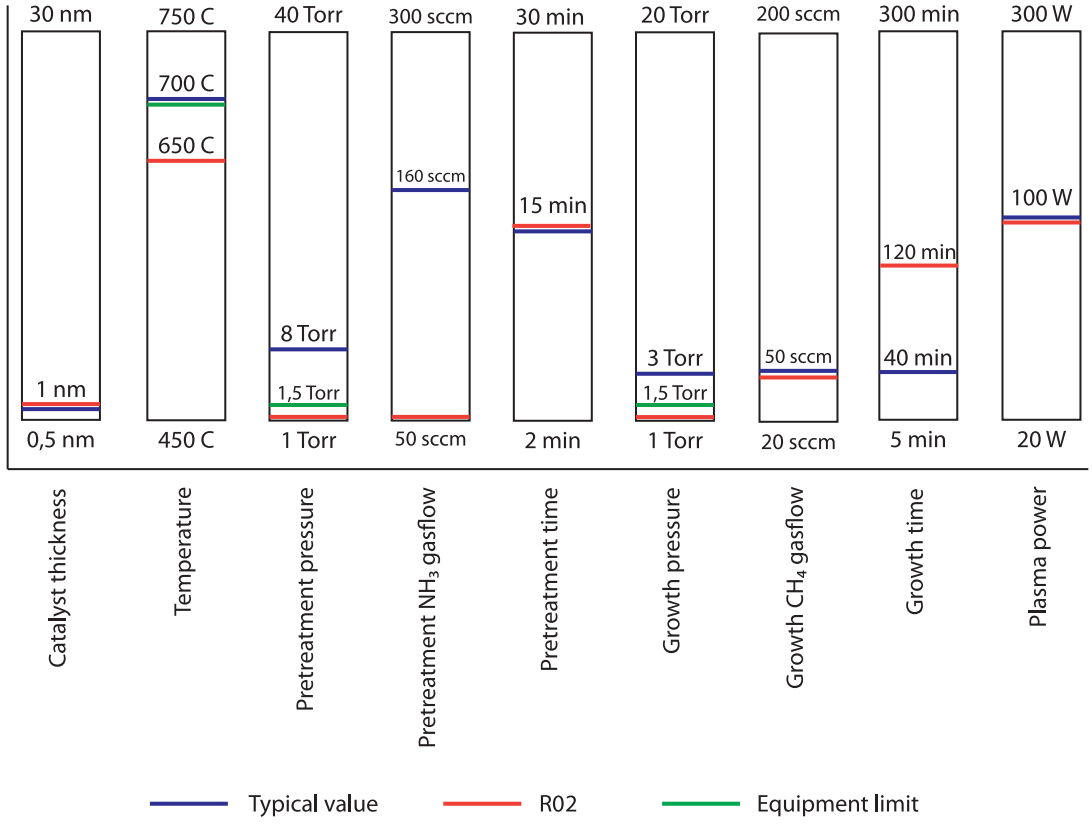


FIGURE 5.14: Illustration of PECVD Parameters. The boxes illustrate the parameter domain for typical VACNT growth with the same setup of gases and equipment. Blue lines represent the most common values in literature while the green lines are the equipment limitations. Red lines indicate the settings of recipe R02.

5.5 Concluding Remarks

Even though the fabrication was well planned, unexpected issues with equipment and lack of experience destroyed several samples. The total pretreatment time including chamber preparation time is identified as a particularly sensitive parameter. It is also shown that optical microscopy provide an easy and inexpensive way of detecting VACNTs. Despite the difficulties, it is believed that CNTs were grown at a maximum length of 6,6 µm. The length is not as long as desired to be able to make CNT yarn or fabric.

5.6 Further Work

The fabrication provided only a fraction of the desired length to achieve yarn or fabric pulling. It was therefore decided, with respect to the hazards of airborne CNTs and the unlikely success, the attempt of pulling should be left out. The fabrication technique of VACNT should be improved before such attempts are made.

Because the technique has proven to be successful for other research groups, there is no need to stop the device development. A cost analysis of the fabrication should be performed to suggest a retail price once the correct equipment and recipe have been found.

Chapter 6

Cost Analysis

FIGURE 6.1: Norwegian currency [114].

To answer the question of economic feasibility, a cost analysis is performed. This chapter will calculate the expense of a die with VACNTs and the expense per meter of CNT yarn. There will also be an attempt to locate which part of the fabrication is the most costly. The analysis has been done using a modified Cost of Ownership model inspired by the semiconductor industry with formulas thoroughly documented.

6.1 Introduction to Cost Modeling

A common mistake in cost modeling is to calculate the cost as the sum of materials and parts. A more correct approach is to track resources and assign a value for every process step, including equipment, maintenance, facility, labor and so on. Furthermore, cost may also be the lack of profit and the cost of producing faulty goods.

Due to the large uncertainty in the future of nanotechnology, only a manufacturing cost analysis will be performed here, not the full life cycle cost analysis. Depending on what kind of fabrication process used, a Manufacturing Cost Model needs to be selected [115]. Analysis approaches include Process-Flow Analysis, Cost of Ownership (COO), Activity Based Costing (ABC) and Parametric Models. The Cost of Ownership model, partly developed by Intel (Fig. 6.2), is identified as the most suitable model as it is focused on the cost of equipment, facilities and processes, considerable expenses in the fabrication of CNTs.

FIGURE 6.2: Fabrication facility at Intel, one of the founders of the Cost of Ownership analysis [116].

In the mid 1980s, the semiconductor industry had trouble calculating the cost of defects and idle time of their expensive fabrication equipment [117]. The products required very little material, were high in volume and had a very short lifetime before becoming obsolete. As a result, the COO model was developed to predict the cost per unit. The fundamental COO algorithm (Eq. 6.1) is dividing the total cost throughout the lifetime on the total number of good units produced during the lifetime.

$$\mathrm{COO} = \frac{\mathrm{CF} + \mathrm{CV} + \mathrm{CY}}{\mathrm{T} \cdot \mathrm{Y} \cdot \mathrm{U}} \tag{6.1}$$

where:

CF	is the fixed costs occurring once.
CV	is the variable costs occurring regularly.
CY	is the cost of failed parts.
T	is the throughput.
Y	is the yield.
U	is the utilization.

6.2 Method

The cost analysis will be based upon the fabrication procedure in section 5.2. To fit the current scenario, the Cost of Ownership model needs to be adapted. It must be able to calculate the loss of profit from having a machine running as a bottleneck, but also give a reliable prediction of the expense put into the product. Firstly, some key terms are defined:

Cost - The sum of money spent on the product and the money saved or lost.

Cost of yield (omis) - Difference between cost and yielded cost calculated by the *Omission method*.

Cycle time - The time between each finished unit.

Expense - Actual money being spent on the product.

Expense of yield (cuml) - Difference between expense and yielded expense calculated by the *Cumulative method*.

Good unit - A unit with no defects.

Labor burden - Added fraction on the hourly labor rate to account for business management, fringe benefits, etc. Total labor rate is (1 + labor burden).

Profit - Expected profit from selling each unit.

Step yield - Fraction of good units in the output of a step.

Yielded cost - Effective cost per finished unit with no defects (good unit), i.e. cost divided by yield.

Yielded expense - Effective expense per finished unit with no defects (good unit), i.e. expense divided by yield.

Some operational assumptions are made.

- Defects may not be discovered or repaired during the fabrication process.
- All produced units will be sold immediately, i.e. no stockpiling.

6.2.1 Equations

The following section explain the formulas used in the cost analysis. It is common to divide the calculation into three parts called capital costs, sustainment costs and performance costs [118]. This analysis will also calculate capital expense, sustainment expense and performance expense. The cost may be used to identify uneconomical parts of the fabrication and the expense may be used to calculate retail price. All formulas employed here are modified versions of the formulas found in *Cost Analysis of Electronic Systems* by Prof. Sandborn [118].

Capital Cost/expense

The cost of acquiring the equipment is calculated as capital cost. It is a one time cost and may be reduced by selling the equipment after its use. Here, the expense and cost is the same.

$$\text{Capital Cost/expense} = \frac{\text{Purchase Price} - \text{Residual Value}}{\text{Depreciation Life}} \tag{6.2}$$

where:

Purchase Price	is the cost of buying, installing and configuring the machine.
Residual Value	is value of the machine at the end of its depreciation life.
Depreciation Life	is how many years the machine is expected to operate.

Sustainment Cost/expense

The sustainment expense is the sum of scheduled and unscheduled maintenance cost, including the repair of equipment. The sustainment cost also includes the lost profit from unscheduled maintenance events.

Typical scheduled maintenance events are cleaning, change of seals and calibration. Spare parts are included in the labor burden.

$$\text{Scheduled maintenance} = N_{sch} \cdot T_R \cdot \text{LR} \tag{6.3}$$

where:

N_{sch}	is the number of scheduled shutdowns for maintenance per year.
T_R	is the avg. hours used to perform the maintenance.
LR	is the hourly labor cost including labor burden.

Machines have a predicted number of operating hours before something fails and require an unscheduled maintenance event.

$$\text{Unscheduled maintenance} = \frac{T_{prod}}{\text{MTBF}} \cdot \text{MTTR} \cdot \text{LR} \tag{6.4}$$

where:

T_{prod}	is the number of production hours per year.
MTBF	is the mean time between failures.
MTTR	is the mean time to repair a failure.
LR	is the hourly labor cost including labor burden.

The unscheduled maintenance events were supposed to bring profit but is now lost profit from downtime.

$$\text{Lost profit from dt.} = \frac{\frac{T_{prod}}{\text{MTBF}} \cdot \text{MTTR}}{\text{Cycle time}} \cdot \text{Profit} \tag{6.5}$$

where:

T_{prod}	is the number of production hours per year.
MTBF	is the mean time between failures.
MTTR	is the mean time to repair a failure.

Performance Cost/expense

Performance expense includes the expense of labor, materials, facility and the expense of yield. Performance cost includes expense of labor, materials, facility, cost of yield, lost profit from scraped units and the cost of having a bottleneck machine.

Labor cost is the cost of operating the equipment.

$$\text{Labor cost} = T_{step} \cdot T_{prod} \cdot \text{LR} \tag{6.6}$$

where:

T_{step}	is the labor time per unit.
T_{prod}	is the number of production hours per year.
LR	is the hourly labor cost including labor burden.

Material expense is the expense of material and parts not included in the facility expense.

$$\text{Material expense} = \text{Unit material expense} \cdot \text{Units per year} \tag{6.7}$$

The facility expense is the expense of infrastructure like utilities and standard supplies.

$$\text{Facility expense} = \text{Monthly facility expense} \cdot 12 \tag{6.8}$$

The expense of yield may be understood as how much you need to pay extra to reproduce the defect units such that all units are good. The expense of yield is calculated by the cumulative method, hence the sum of all the steps expense of yield should be the total expense of yield for one finished unit.

$$\text{Expense of yield, step i} = \text{EOO}_i - \text{EOO}_{\min,i} \tag{6.9}$$

$$= \left(\frac{\sum_{n=1}^{i} \text{EOO}_{\min,n}}{\prod_{n=1}^{i} Y_n} - \frac{\sum_{n=1}^{i} \text{EOO}_{\min,n-1}}{\prod_{n=1}^{i} Y_{n-1}} \right) - \text{EOO}_{\min,i} \tag{6.10}$$

where:

EOO_i	is the expense of ownership including reproduction of defect units for step i, i.e. yielded cost by the cumulative method.
$\mathrm{EOO}_{\mathrm{min},i}$	is the expense of ownership for a perfect machine without defects.
Y_i	is the yield of step i.

The cost of yield also includes the fabrication cost from previous and succeeding steps when a step produces a defect. That is, the cost of sputtering a sample that is going to be ruined in the PECVD anyways is assigned as a PECVD cost. To achieve this, the omission method is used. However, the cost of yield per step may *not* be summed to find total cost of yield for one finished unit due to overlapping costs. The cost of yield is a true measure on the step cost and may be used to identify costly machines.

$$\text{Cost of yield, step i} = \mathrm{COO}_i - \mathrm{EOO}_{\mathrm{min},i} \tag{6.11}$$

$$= \left(\frac{\sum_{n=1}^{\infty} \mathrm{EOO}_{\mathrm{min},n}}{\prod_{n=1}^{\infty} Y_n} - \frac{\left(\sum_{n=1}^{\infty} \mathrm{EOO}_{\mathrm{min},n} \right) - \mathrm{EOO}_{\mathrm{min},i}}{\left(\prod_{n=1}^{\infty} Y_n \right) / Y_i} \right) - \mathrm{EOO}_{\mathrm{min},i} \tag{6.12}$$

where:

COO_i	is the cost of ownership including reproduction of defect units and cost from preceding and succeeding steps, i.e. yielded cost by the omission method.
$\mathrm{EOO}_{\mathrm{min},i}$	is the expense of ownership for a perfect machine without defects.
Y_i	is the yield of step i.

Every defect unit was supposed to give a profit, but is now a cost of lost profit.

$$\text{Lost profit from defects} = (1 - \text{Step yield}) \cdot \text{Units per year} \cdot \text{Profit} \tag{6.13}$$

If one step has a lower cycle time than the rest of the steps it will perform as a bottleneck delaying the total cycle time. Such a machine will then be assigned a

bottleneck penalty cost.

$$\text{Bottleneck penalty} = \left(\frac{T_{prod}}{T_{\text{cycle excl. step}}} - \frac{T_{prod}}{T_{\text{cycle incl. step}}} \right) \cdot \text{Profit} \tag{6.14}$$

where:

T_{prod}	is the number of production hours per year.
$T_{\text{cycle excl. step}}$	is the time of the whole process excluding this step.
$T_{\text{cycle incl. step}}$	is the time of the whole process including this step.

6.2.2 Input Data

Because this analysis is carried out at an early development stage, there is a large uncertainty in the input data. With some contributions from Division Director of NTNU Nanolab and leader of NorFab (Norwegian infrastructure for micro and Nanofabrication.), Dr. Kay Gastinger, estimates of expenses have been made. The inputs regarding equipment yield and maintenance are qualified estimates from own experience gained in the fabrication of VACNTs. The input data in Table 6.1, 6.2 and 6.3 are derived from the following assumptions:

- A year has 52,14 weeks including 2 weeks of holiday, hence 50,14 production weeks.
- The lab is expected to operate 8 hours a day, 5 days a week.
- One unit is the complete spool of CNT yarn pulled from one full wafer of VACNT.
- The expected profit of one unit is iterative calculated according to a profit margin of about 50 %.
- The number of complete square dies of a round wafer is calculated by the *Gross Die Per Wafer* formula by Trapp et al. [119].
- The length and thickness of CNT yarn pulled from a wafer of 100 µm VACNT is 50 m/cm^2 and 2 µm respectively according to Zhang et al. [54].

- The 1 ply yarn is twisted into multiple plies yarn to achieve the desired yarn thickness such that every ply have an effective diameter of 1,5 of its initial diameter.
- The sputtering of Fe and Al are done in the same machine.
- Plasma cleaning of the PECVD is not included in scheduled maintenance events as it may be done outside fabrication hours in an automated process.
- The unit material expense is the expense of 4-inch silicon wafers.

The initial input data are presented in Table 6.1.

TABLE 6.1: First set of input data to the cost analysis.

Parameter	Unit	Value
Production hours per week	h/w	40
Production weeks per year	w/yr	50,14
Cycle time	h	2
Finished units per week	units/w	20
Expected profit	NOK/unit	15 000

6.3 Results

The formulas have been implemented in a Microsoft Excel spreadsheet to do the calculations and can be found in supporting material online. The fabrication is divided into five steps; preparation, sputtering, RTP, PECVD and spinning. The preparation step accounts for unpacking, cleaning and drying of wafers and the spinning step accounts for spinning the yarn onto spools and simple packaging. The yearly cost and expense of ownership are calculated in Table 6.2 and the unit cost and expense of VACNT and CNT yarn are calculated in Table 6.3.

TABLE 6.2: Cost/Expense of Ownership.

		Preparation	Sputter	RTP	PECVD	Spinning
Purchase Price	NOK	50 000	1 200 000	1 200 000	3 000 000	1 500 000
Depreciation life	yr	5	5	5	5	5
Residual value	NOK	-	300 000	300 000	500 000	400 000
Capital cost/expense	**NOK/yr**	**10 000**	**180 000**	**180 000**	**500 000**	**220 000**
Labor rate for maint.	NOK/h	800	800	800	800	800
Labor burden		0,50	2,00	2,00	3,00	2,00
No. scheduled maint. evt.	/yr	2	12	12	12	12
Time per sched. mnt. evt.	h	2	2	2	8	5
Machine MTBF	h	0	1000	1000	1000	1000
Machine MTTR	h	0	24	24	36	24
Scheduled maintenance	NOK/yr	4 800	57 600	57 600	307 200	144 000
Unscheduled maint.	NOK/yr	-	115 523	115 523	231 045	115 523
Lost profit from downt.	NOK/yr	-	361 008	361 008	541 512	361 008
Sustainment cost	NOK/yr	4 800	534 131	534 131	1 079 757	620 531
Sustainment expense	**NOK/yr**	**4 800**	**173 123**	**173 123**	**538 245**	**259 523**
Labor rate for operation	NOK/h	400	400	400	400	400
Labor burden		0,50	0,50	0,50	0,50	0,50
Labor time per unit	h	0,5	2	1	2	1
Cycle time excl. this step	h	2	2	2	2	2
Step yield		0,99	0,95	0,99	0,97	0,98
Unit material expense	NOK/unit	1500	0	0	0	0
Monthly facility expense	NOK/m	10 000	40 000	40 000	60 000	40 000
Labor cost	NOK/yr	300 840	2 406 720	1 203 360	3 208 960	1 203 360
Material expense	NOK/yr	1 504 200	-	-	-	-
Facility expense	NOK/yr	120 000	480 000	480 000	720 000	480 000
Expense of yield	NOK/yr	19 594	308 094	206 338	772 285	556 079
Cost of yield	NOK/yr	391 994	1 047 998	403 448	962 727	556 079
Lost profit from defects	NOK/yr	150 420	752 100	150 420	451 260	300 840
Bottleneck penalty	NOK/yr	-	-	-	-	-
Performance cost	NOK/yr	2 467 454	4 686 818	2 237 228	5 342 947	2 540 279
Performance expense	**NOK/yr**	**1 944 634**	**3 194 814**	**1 889 698**	**4 701 245**	**2 239 439**
Cost of Ownership	NOK/yr	2 482 254	5 400 949	2 951 359	6 922 704	3 380 810
	NOK/unit	2 475	5 386	2 943	6 903	3 371
Expense of Ownership	**NOK/yr**	**1 959 434**	**3 547 937**	**2 242 821**	**5 739 490**	**2 718 962**
	NOK/unit	**1 954**	**3 538**	**2 237**	**5 723**	**2 711**

TABLE 6.3: Final results of the expense of producing VACNT and CNT yarn.

Manufacturing expense		
Total expense, fiber	NOK/yr	16 208 644
Volume, fiber	units/yr	1 003
Expense, fiber	NOK/unit	16 163
Expense, VACNT	NOK/wafer	13 452
Wafer details		
Wafer diameter	inch	≈ 4
Wafer diameter	mm	100
Wafer area	cm^2	78,54
Target die size	cm^2	1,0
Gross Die Per Wafer	dies	50
Fiber details		
Expected fiber length	m/cm^2	50
VACNT height	µm	100
Yarn thickness, 1 ply	µm	2,0
Desired yarn thickness	mm	1,0
Required number of plies		334
VACNT		
Expense of VACNT per area	NOK/cm^2	171
Expense of VACNT per complete die	NOK/die	269
Volume, complete dies	dies/yr	50 140
Fiber		
Expense of fiber, 1 ply	NOK/m	4,12
Expense of fiber at desired thickness	NOK/m	1 375
Volume, 1 ply	km/yr	3 938
Volume, desired thickness	km/yr	12

6.4 Discussion

The expense of 1 ply CNT yarn is calculated at 4,12 NOK/m, making the selling price, with 50% profit margin, about 8,24 NOK/m. However, the yarn is only 2 µm thick, hence hard to handle. If spun to a diameter of 1 mm the price skyrockets to 1 375 NOK/m. It is believed that growth of longer CNTs on the wafer will increase the diameter of the 1 ply yarn, but the cost of macroscale yarn will still be very high. This result support the presumption that CNT yarn is most suited in low quantities.

Aldrich Materials Science are selling square dies of PECVD grown VACNTs for about 10 000 NOK/die [49]. The calculated expense of fabricating one wafer of VACNTs is 13 452 NOK making the expense per die as little as 269 NOK. In today's market, selling dies of VACNTs is therefore much more lucrative than selling CNT yarn. However, it is assuming you are able to sell 50 000 dies per year which is unlikely. Before entering this market, a thorough analysis of the market demand is necessary.

The calculation of cost, including loss of profit, identifies the PECVD and the sputter coater as the most costly equipment. They are expected to have a low yield because successful growth is very dependent on their parameters. The defects need to be replaced by producing new units and the profit of selling the defected units vanish. When selecting machines for this kind of fabrication facility, the machine yield is a crucial parameter.

6.5 Concluding Remarks

The Cost of Ownership model has been altered to calculate both real expenses and simulated costs for the fabrication of VACNT and CNT yarn. The expense of 1 ply, 2 µm thick, CNT yarn is 4,12 NOK/m and the expense of a 1x1 cm square die of VACNT is 269 NOK/die. The defects caused by the PECVD and the sputter coater are the most costly and could be reduced by increasing the machine's yield.

Chapter 7

Evaluation

FIGURE 7.1: A moment of afterthought at NTNU Nanolab.

The fundamental steps of product development using push innovation have been completed. Each chapter is to be evaluated to discuss its outcome and lessons learned. Furthermore, some thoughts of how they may be improved are proposed.

Material Potential

Founding this project on carbon nanotubes made the search for material properties an easy task as scientific journals are flooded with papers on the topic. However, it was discovered that as the CNTs got refined into macroscale structures, the material properties weaken and fluctuate a lot. The tensile strength of a single CNT is measured at 100 GPa while the CNT yarn is less than 1 GPa. Median values for CNT yarn properties are considered most reliable and are summarized in Table 7.1. It recommended that material specifications are held back until the prototype is fabricated and tested.

Table 7.1: Median values of CNT properties.

Property	Median	Unit
CNT Diameter	10	nm
CNT Length	650	µm
Yarn Twist	25 000	turns/m
Yarn Diameter	10	µm
Density	0,68	g/cm^3
E-Modul	65	GPa
Tensile strength	625	MPa
Tenacity	1,72	N/Tex
Elongation at break	2,43	%
Toughness	21	J/g
Electric conductivity	410	S/cm
Thermal conductivity	43	W/m·K

Locating Applications

The industry partners showed hesitation for investing time and resources in this project. Despite efforts to brag of the excellent material properties, they wanted to see physical results. The best approach would probably be to make a strip of CNT yarn and mold it inside a piece of epoxy. Bringing the sample as well as documenting and presenting the material test results would give more enthusiasm by companies. Nevertheless, some ideas emerged which are listed in Table 7.2.

TABLE 7.2: Potential business ideas in marine and offshore oil/gas.

Business ideas
Mooring knot
Net cage
Ropes
HVAC thermal wheel
Thruster components
Buoyancy body
Anti-icing coating
Oil/Water separation

Concept Development

The net cage is an example of how CNTs are ideal for load bearing structures in a challenging environment (Fig. 7.2a). However, high performance polymer fibers like Dyneema are still outperforming commercial CNT yarn. If CNT yarn is to raise the standard, it needs to prove a long lifetime and anti-fouling properties. Moreover, the biggest obstacle, the issue of health risk, need to be addressed and solved. This is a task for scientists and researchers and should not be attempted by commercial companies because the customer want scientific consensus, not internal reports.

The oil drier employs the functional properties of the nanostructures to separate water from oil (Fig. 7.2b). The contact angle of oils are low, letting the oil suffuse and penetrate, whereas the contact angle of water is high such that droplets keep their shape and cannot penetrate. The product is novel and probably patentable. Because the CNTs are in a closed system, the environmental risk is minor. The problem with the oil drier is the lack of proof that it will work. A prototype needs to be made and tested on various commercial hydraulic and lubricating oils.

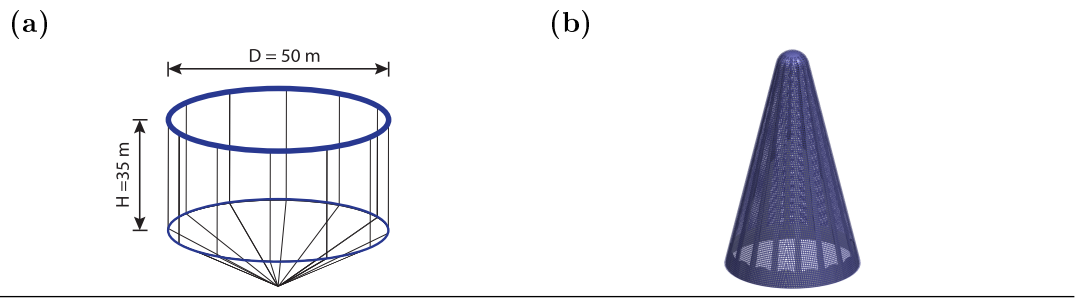


FIGURE 7.2: **(a)** Illustration of a net cage arrangement for fish farming including typical measurements. **(b)** Illustration of complete CNT filter unit with CNT membrane.

Fabrication

The fabrication of CNTs was unsuccessful as the goal of growing 100 µm long tubes and pulling a yarn from them was not achieved (Fig. 7.3). This made the task of testing CNTs eligibility as stated in the project task fail. One reason is that the applied PECVD was not optimal for CNT fabrication. The majority of CNTs are grown by CVD that require higher temperatures and pressures than the PECVD could provide as well as other process gasses. More time would be needed to work the chamber parameters to find an optimal recipe. Leading over to the second reason, experience. The experience in growing carbon nanotubes in the research group and at NTNU Nanolab is limited. If the concepts proposed here are to be continued, it would be wise to seek help from more scientists.

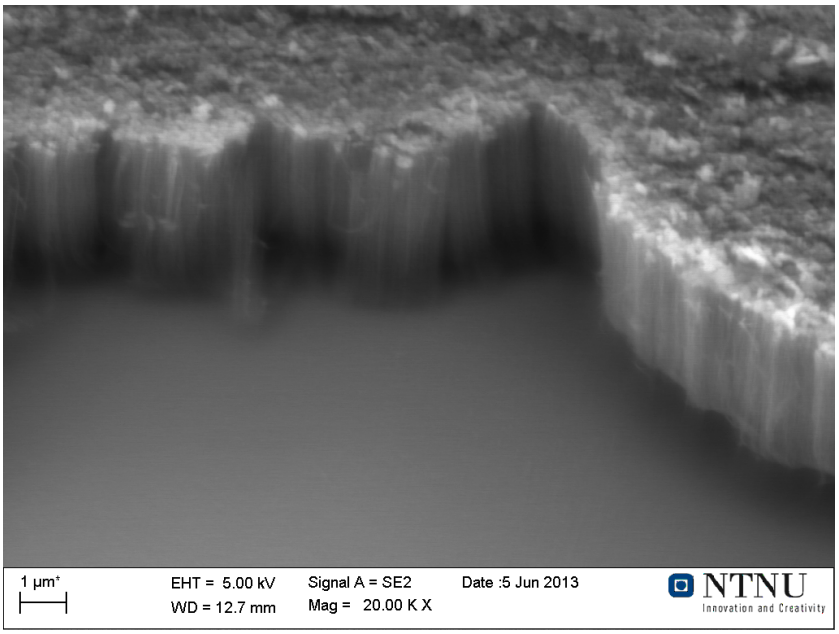


FIGURE 7.3: SEM image of sample R02 yielding the tallest vertically alligned CNTs measuring 6,6 µm.

Cost Analysis

The cost analysis showed the cost of producing VACNTs are much less than the market price when assuming a perfect demand. The equipment is expensive and is best utilized if the demand is steady and high. It also showed how the price of CNT yarn increased as it was scaled from one-ply yarn to a 1 mm diameter rope. A lesson from this is that the production of VACNTs is much more feasible than CNT yarn as seen in Fig. 7.4. Furthermore, applications which require low quantities of CNTs should be prioritized.

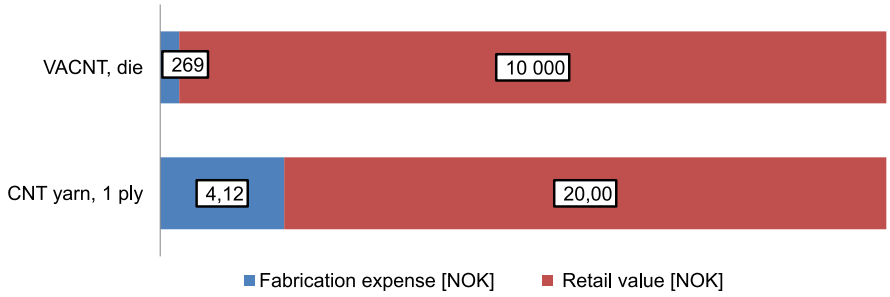


FIGURE 7.4: Results from cost analysis showing how selling dies with VACNT is much more lucrative than selling CNT yarn. Values in Norwegian Krone.

Timing

The introduction of a new technology to the commercial market should always be taken with great care. There is no guarantee being first is the most profitable. On the contrary, being first impose a lot of risk including the cost of convincing the public the technology is safe. A close look at the current public acceptance of nanomaterials is necessary before introducing a new product.

Make or Buy?

An important question for companies developing applications with carbon nanotubes is whether to make the CNTs yourself or buy them? The high market price and the sensitivity of the properties on the growth procedure suggest the developers to fabricate their own CNTs. Whereas the manufacturers of CNTs should also invest in finding possible uses for their own product to increase the demand and make it more predictable.

National Interest

The potential of carbon nanotubes show similarities to the broad use of semiconductors. There are few countries leading the semiconductor development giving fruit to large industries in electronics. It would therefore definitely be of national interest for any country making a leading position in carbon nanotube technology because it may nourish export and make jobs.

In the 70's, five microelectronic companies founded the Semiconductor Industry Association (SIA). The American technological advance and profit in microelectronics is much thanks to this cluster. If a similar knowledge transfer forum is established among Norwegian maritime companies, with sharing of knowledge

and resources on nanotechnology, the probability of success is much higher. In fact, such a cluser already exist in Norway called NCE Micro- and Nanotechnology [120]. The work focus on MEMS (micro-electro-mechanical-systems) and sensors, but innovation in all industries are welcome.

Applicability in Maritime Applications

Carbon nanotubes are well suited the maritime industry in Norway. The CNTs have great environmental stability making them robust without deteriorating in salt and humid conditions. They are strong, light weight and possibly anti fouling. Furthermore, the maritime industry is a big employer all along the Norwegian coast which existence is dependent on providing high-end and international competitive technology. They are likely to invest in new technology provided that a proof of concept has been made.

Stage Model

The development of carbon nanotube technology using a push innovation stage model is a reasonable approach as it provided a broad specter of business ideas. If this project were to be redone, the same procedure would have been employed. It is found that the communication in step II, sharing (Locating applications), is of particular importance as it is the breeding ground for good ideas.

Chapter 8

Conclusion

Two business concepts, net cage and oil drier, have been developed to solve issues with current technology by the use of carbon nanotubes (CNTs). The net cage is made of a CNT yarn to reduce the risk of rupture, reduce maintenance and increase the lifetime. However, due to health risks, this device should be put on hold. The oil drier is composed of a membrane made of CNT fabric wrapped around a cone. The membrane is superhydrophobic stopping water and superoleophilic letting oil pass through. Such a device provides a novel solution to water contamination in hydraulic and lubricating systems and is considered most viable.

Fabrication of carbon nanotubes is a delicate process. About 6,6 µm long vertically aligned CNTs have been grown, but the minimum requirement to make CNT yarn or fabric is 100 µm. Lack of time, experience and equipment limitations were identified as causes. The expense of fabricating VACNT and CNT yarn was calculated to be about 269 NOK/die and 4,12 NOK/m respectively using a Cost of Ownership model.

The Norwegian aquaculture, shipping and offshore oil/gas industries are continuously searching for new ideas to keep a cutting edge in the global market. The exceptional properties of carbon nanotubes, such as high strength, low weight and corrosion resistance, indicate an excellent future in maritime applications.

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Appendix A

Magnified Flyer for Offshore Oil/Gas Industry

FIGURE A.1: Flyer sent out to potential business partners to attract ideas from the offshore oil/gas industry. Copy found in supporting material online.

Appendix B

CNT Yarn Characteristics from Literature

Characteristics and properties of CNT yarn made by pulling from CNT array have been collected from various research papers. Results are presented in Table B.1 and B.2. Mean and median values are calculated and presented in Table B.3.

TABLE B.1: Characteristics and properties of CNT yarn made by pulling from CNT array - part I.

	CNT Characteristics		Yarn Characteristics		Yarn Properties							
Ref.	Diam. [nm]	Length [μm]	Twist [turns/m]	Yarn Diam. [μm]	Density [g/cm^3]	E-Modul [GPa]	Tens. strength [MPa]	Tenacity [N/Tex]	Elong. at brk. [%]	Toughn. [J/g]	El. cond. [S/cm]	Therm. cond. [W/m·K]
a	10	300		8,5	0,80						250	26
b		300		10,0			500			21,0		
c		550		10,0		10	700		5,9	27,0		
d	15	500	10 000	22,0	0,90						600	60
e	10,5	5000		40,0		7	280					
f	15	450										
g	10	425	5 150	14,0	0,98	95	1 750	1,79	1,4		920	
h	10	235		19,0		56	850		2,3		900	
i		170		6,0			500					
j	8	350		13,0			1 000				550	
k	5,5	720	10 000	16,6	0,53	32	550	1,04	7,6			
l	5,5	720	10 000	17,1	0,55	65	910	1,65	1,5			
m	5,5	720	10 000	17,1	0,55	120	2 200	4,00	1,6			
n	8	350	150 000	32,0			1 185		6,5		270	
o	8	350	75 000	17,5		147	1 800		2,0			
p	11,5	100	80 000	5,5	0,80	18	305	0,38	10,1	15,5	300	
q	7	1000	40 000	4,9	0,20	182	2 325	11,74	9,0	542,5		
r	10	650	40 000	4,0		275	850		2,2		170	
s	10	650	40 000	13,0		89	170		1,8		170	
t	10	650	60 000	3,0		330	1 910		7,0		410	
u	10	650	60 000	10,0		241	410		2,4		410	
v	10	1000		10,0		25	350		2,2	5,0	500	
w	10	1000	1 000	10,0		10	400		5,0	11,0		
x	10	1000	1 000	10,0		8	500		11,0	30,0		
y				62,5	0,75		900	1,20	17,5		650	

Table B.2: Characteristics and properties of CNT yarn made by pulling from CNT array - part II.

Ref.	Composition	Full reference
a	Pure CNT	Aliev et al. 2007 [99]
b	Pure CNT	Atkinson et al. 2007 [100]
c	Pure CNT	Atkinson et al. 2007 [100]
d	Pure CNT	Jakubinek et al. 2012 [101]
e	Pure CNT	Jayasinghe et al. 2011 [102]
f	Pure CNT	Kuznetsov et al. 2011 [97]
g	CNT / PVA	Liu et al. 2010 [103]
h	Pure CNT	Liu et al. 2010 [104]
i	Pure CNT	Nakayama 2008 [105]
j	CNT / particles	Randeniya et al. 2010 [106]
k	Pure CNT	Ryu et al. 2011 [107]
l	CNT / PEI-C	Ryu et al. 2011 [107]
m	CNT / PEI-C	Ryu et al. 2011 [107]
n	Pure CNT	Tran et al. 2009 [108]
o	CNT / PU	Tran et al. 2011 [109]
p	Pure CNT	Zhang et al. 2004 [54]
q	Pure CNT	Zhang et al. 2007 [86]
r	Pure CNT	Zhang et al. 2007 [110]
s	Pure CNT	Zhang et al. 2007 [110]
t	Pure CNT	Zhang et al. 2007 [110]
u	Pure CNT	Zhang et al. 2007 [110]
v	Pure CNT	Zhang et al. 2008 [111]
w	Pure CNT	Zhang et al. 2008 [111]
x	Pure CNT	Zhang et al. 2008 [111]
y	Pure CNT	Nanocomp Technologies Inc. [56]

Table B.3: Typical characteristics for CNT yarn pulled from CNT array. Mean and median values of Table B.1.

Property	Mean	Median	Unit
CNT Diameter	10	10	nm
CNT Length	760	650	µm
Yarn Twist	37 009	25 000	turns/m
Yarn Diameter	14	10	µm
Density	0,66	0,68	g/cm^3
E-Modul	101	65	GPa
Tensile strength	922	625	MPa
Tenacity	3,43	1,72	N/Tex
Elongation at break	4,68	2,43	%
Toughness	93	21	J/g
Electric conductivity	445	410	S/cm
Thermal conductivity	43	43	W/m·K

Appendix C

Complete CNT Recipes

Full procedure for reference recipe RO1 found in Table C.1. Complete details for all recipes found in Table C.2.

Table C.1: Complete recipe - R01.

Step	Description	Equipment	Parameters
1	Cut sample	Dynatex DXIII scriber	5x5 mm of a 250 µm thick, 2-inch Si-wafer
2	Clean sample	Ultrasonic bath / Solvent bench	Acetone in ultrasonic bath, 5 min, 20 °C → Ethanol bath → Spray with isopropanol → Spray with DI-water → N2 blow dry
3	Dehydrate sample	Hot plate (located at end of 5th "finger")	Desired temp: 185 °C. Thermostat show deviation of -65 °C. Setpoint: 250 °C, 5 min.
4	Deposit barrier layer	Cressington 308R Sputter and Evap.	30 nm Al by sputtering, Water-cooled head (#1), Tooling factor: 6,01, Density: 2,70, Rotational speed: "1 o'clock", Pressure: $3,0 \cdot 10^{-5}$ Torr, Argon flow rate: N/A, Current: 80 mA.
5	Oxidize barrier layer	JetFirst 200 RTP	500 °C, 500 sccm O_2, 30 min, 1000 mTorr
6	Deposit catalyst	Cressington 308R Sputter and Evap.	1 nm Fe by sputtering, Non-cooled head (#2), Tooling factor: 6,01, Density: 7,87, Rotational speed: "1 o'clock", Pressure: $3,0 \cdot 10^{-5}$ Torr, Argon flow rate: N/A, Current: 80 mA.
7	Chamber preparation	Oxford Instr. PlasmaLab System 100 PECVD	Preheat unit to 650 °C. Purge N_2 2 min - Pump 22 min ($1,51 \cdot 10^{-5}$ Torr)
8	Catalyst pretreatment		Add 50 sccm NH_3 at 1000 mTorr for 30 min, 650 °C
9	CNT growth		650 °C, 50 sccm CH_4, 1000 mTorr, 100 W, 120 min
10	Chamber dispatch		(Pump 3 min - Purge N_2 2 min) x 3 → Pump to $5,54 \cdot 10^{-6}$ Torr (7 min), Temp. drop to 425 °C

Table C.2: Complete details for all recipes.

Parameter	R01	R02	R03	R04	R05	R06	R07	R08
Fe thickness [nm]	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Al thickness [nm]	35,0	35,0	30,0	30,0	30,0	30,0	30,0	30,0
RTP gas	O_2	O_2	O_2	O_2	O_2	O_2	O_2	O_2
RTP gasflow [sccm]	500	500	500	500	500	500	500	500
RTP pressure [Torr]	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
RTP temp [°C]	500	500	500	500	500	500	500	500
RTP time [min]	30	30	30	30	30	30	30	30
PECVD start temp [°C]	650	300	650	650	650	650	650	650
Ch. prp. purge time [min]	2	2	2	2	2	2	2	2
Ch. prp. pump-t-b time [min]	22	3	10	99	7	7	10	10
Ch. prp. base press. [10^{-6} Torr]	15,0	5,0	9,7	5,0	8,6	8,1	7,6	14,0
Pretreatment gas	NH_3	NH_3	NH_3	NH_3	NH_3	NH_3	N_2O	N_2O
Pretreatment gasflow [sccm]	50	50	50	50	50	50	50	50
Pretreatment pressure [Torr]	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Pretreatment temp [°C]	650	650	650	650	650	650	650	650
Pretreatment time [min]	30	15	30	45	48	48	30	30
Growth gas	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4
Growth gasflow [sccm]	50	50	50	50	50	50	50	50
Growth power [W]	100	100	100	100	100	100	100	100
Growth pressure [Torr]	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Growth temp [°C]	650	650	650	650	650	650	650	650
Growth time [min]	120	120	120	60	120	60	60	120
Ch. dsp. pump x3 [min]	3	3	3	3	3	3	3	3
Ch. dsp. purge x3 [min]	2	2	2	2	2	2	2	2
Ch. dsp. cooling time [min]	0	0	0	0	0	0	38	39
Ch. dsp. pump-t-b time [min]	7	7	6	7	6	6	1	2
Ch. dip. temp [°C]	435	419	436	412	422	425	300	300
Opt.M. measured height [µm]	0	8	0	3	6	0	2	5
SEM measured height [µm]	0,0	6,6	0,0	1,1	3,4	0,0	1,2	2,4
CNT observed?	Yes	Yes	-	Yes	Yes	-	Yes	Yes
VACVT observed?	No	Yes	-	No	Yes	-	Yes	Yes

Appendix D

Fabrication Equipment

The entire CNT fabrication was carried out in cleanroom grade ISO7 except PECVD at ISO5, both at NTNU Nanolab. A short presentation of the equipment used in the fabrication follows.

Dynatex DXIII Scriber

The scriber is used to cut the wafer into smaller samples. It uses a diamond tip to scribe along the cutting edge and then hit the cut with a bar, cleaving it [121]. The scriber can maximum cut a gap width of 5 µm and at a rate of 75 mm/s. The breaker uses an impulse bar and can do 2 breaks/s.

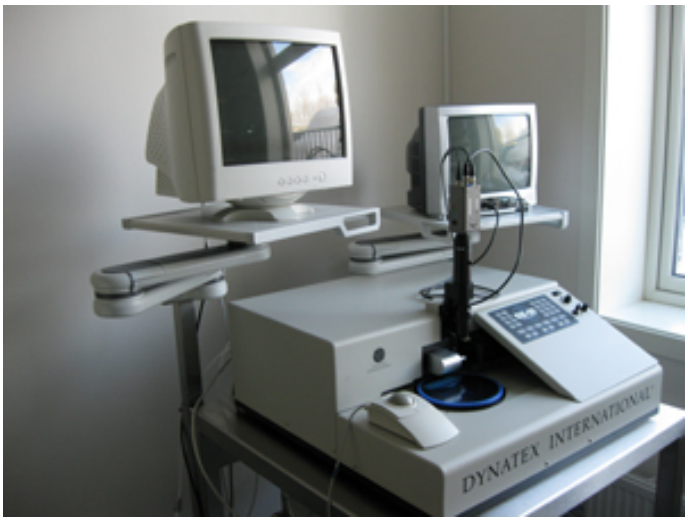

FIGURE D.1: Photograph of Dynatex DXIII Scriber [121].

Ultrasonic bath

An ultrasonic bath is used to clean the wafer after scribing. It uses sound waves to oscillate the liquid molecules causing cavitation on the sample surface tearing off contaminants.

FIGURE D.2: Photograph of ultrasonic bath.

Hot plate

A hot plate is a very accurate and leveled heated plate used to dehydrate the wafer after cleaning.

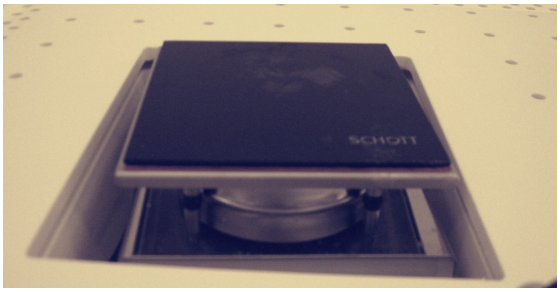

FIGURE D.3: Photograph of hot plate.

Jipilec JetFirst 200 RTP

RTP, short for rapid thermal processing, is an oven used for annealing, oxidation, crystallization, etc., under a controlled atmosphere or vacuum [121]. It contains sixteen 6 000 W halogen lamps that can heat at a rate of 100 °C/s up to a temperature of 1 200 °C. Two process gases are connected, O_2 and N_2.

FIGURE D.4: Photograph of Jipilec JetFirst 200 RTP.

Cressington 308R Sputter and Evaporator

The instrument is used to deposit thin films of various materials. The atoms are detached from a target either by bombarding the target with argon ions (sputtering) or by heating the target by resistive heating until it evaporates [121]. The substrate is located above the target on a rotating stage at which the atoms redeposit. The unit has two DC magnetron sputter heads, one of which is water cooled and two water cooled evaporation boats. A quartz crystal is used to measure the film thickness.

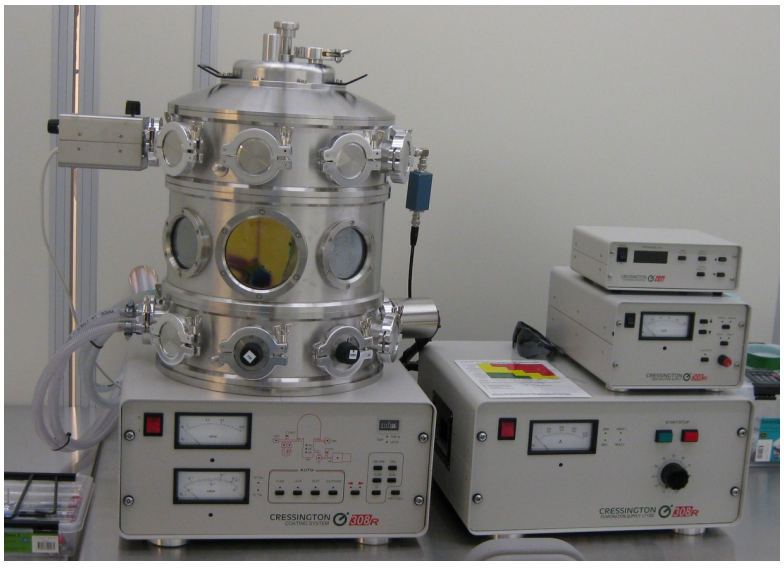

FIGURE D.5: Photograph of Cressington 308R Sputter and Evaporator.

Oxford Instruments PlasmaLab System 100 PECVD

The instrument is used to deposit thin films at a very accurate rate by plasma-enhanced chemical vapor deposition. The plasma may be stroked from the top electrode by a RF source (13,56 MHz), a LF source (50 – 460 KHz) or a mixture of the two [121]. A bottom DC electrode (10 – 20 V) absorb the electrons. The sample is placed on a heated stage with a minimum temperature of 20 °C and a maximum temperature of 700 °C. The unit is connected to a variety of process gasses including SiH_4, NH_3, N_2O, N_2, Ar, CF_4, CH_4, 10%PH_3/Ar and 10%B_2H_6/Ar.

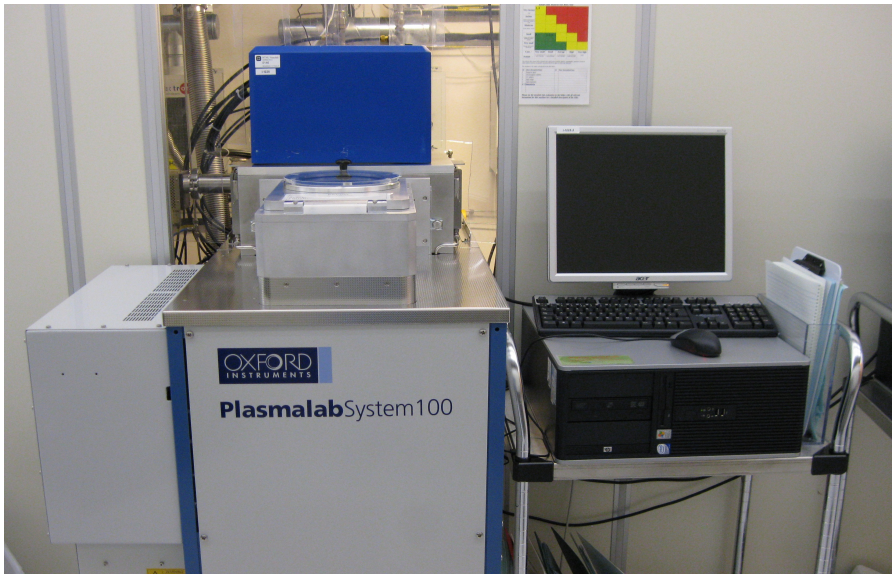

FIGURE D.6: Photograph of Oxford Instruments PlasmaLab System 100 PECVD.

Zeiss AxioScope A1 for Reflected light BF-DIC/POL

An optical microscope with a color CCD-camera of 3,3 megapixels [121]. The microscope is installed with a differential interference contrast illumination to improve pictures of nearly transparent samples.

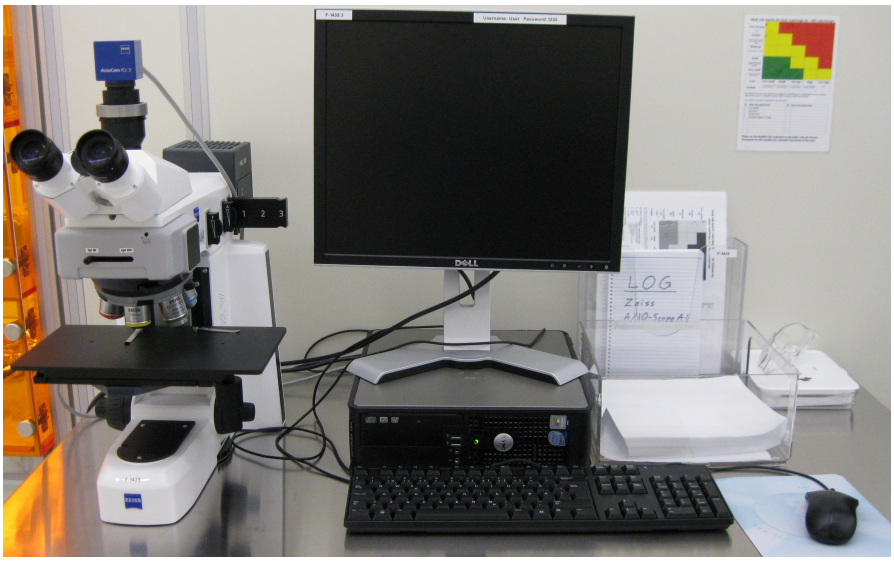

FIGURE D.7: Photograph of Zeiss AxoScope A1 for Reflected light BF-DIC/POL

Hitatchi TM3000 Tabletop SEM

The tabletop SEM is a small and simple unit for scanning electron microscopy (SEM). It uses low vacuum and can magnify an area 15 to 30 000 times [121]. It is suitable for quick imaging of microscale structures.

FIGURE D.8: Photograph of Hitatchi TM3000 Tabletop SEM.

FEI Helios NanoLab DualBeam FIB

FIB is short for focused ion beam and is used to machine samples by sputtering with Ga-ions [121]. The instrument also has an electron beam for SEM of which

the resolution may reach 1,2 nm in optimal conditions. The instrument was used for imaging purposes.

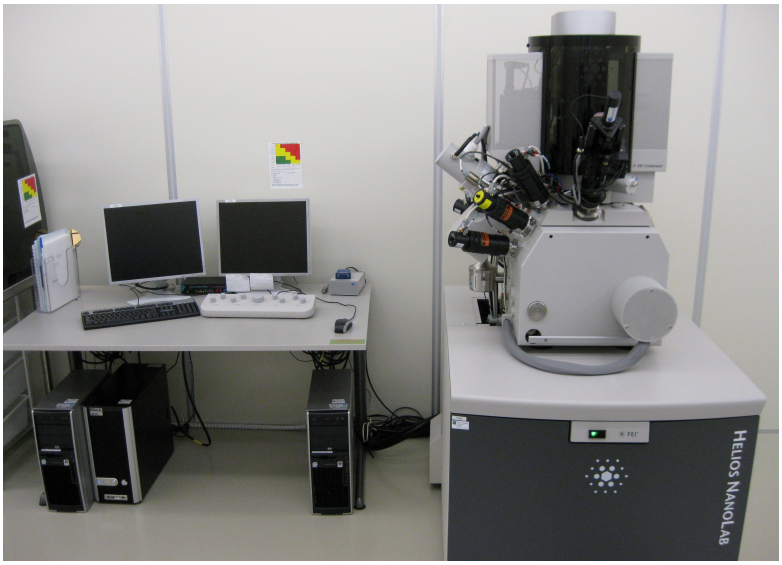

FIGURE D.9: Photograph of FEI Helios NanoLab DualBeam FIB.

Zeiss Ultra 55 LE FE-SEM)

The electron microscope is equipped with a field emission cathode for high resolution imaging [122]. The unit can run at an acceleration voltage of 0,02 – 30 kV, magnification of 12 – 1 00 000 times and may reach a resolution of 0,8 nm in optimal conditions.

FIGURE D.10: Photograph of Zeiss Ultra 55 LE FE-SEM.

Appendix E

Handling and Storage of CNTs

Throughout the fabrication, there are several ways of harming the sample, equipment, facility, coworkers and oneself, hence risk assessment and mitigation is important. All users of the cleanroom are required to attend a cleanroom introduction and HSE course, receive training in operating the equipment and to fill out a risk evaluation form.

In addition to regular safety routines, the work with CNTs should act in accordance with the following guidelines:

- Waste that might contain CNTs should be collected in a separate container.
- Whenever risk of releasing airborne CNTs, the work should be done inside a fume hood with gloves and mask with P2/P3 particle filter.
- Storing of CNTs must be done in a ventilated cabinet. Sample boxes must be marked with activity number, name, content and appropriate warning labels.
- In accordance with Norwegian legislation, work with CNTs must be logged for future reference.

Figure E.1 shows the storage box used to store the samples in the lab. It was kept in a ventilated cabinet.

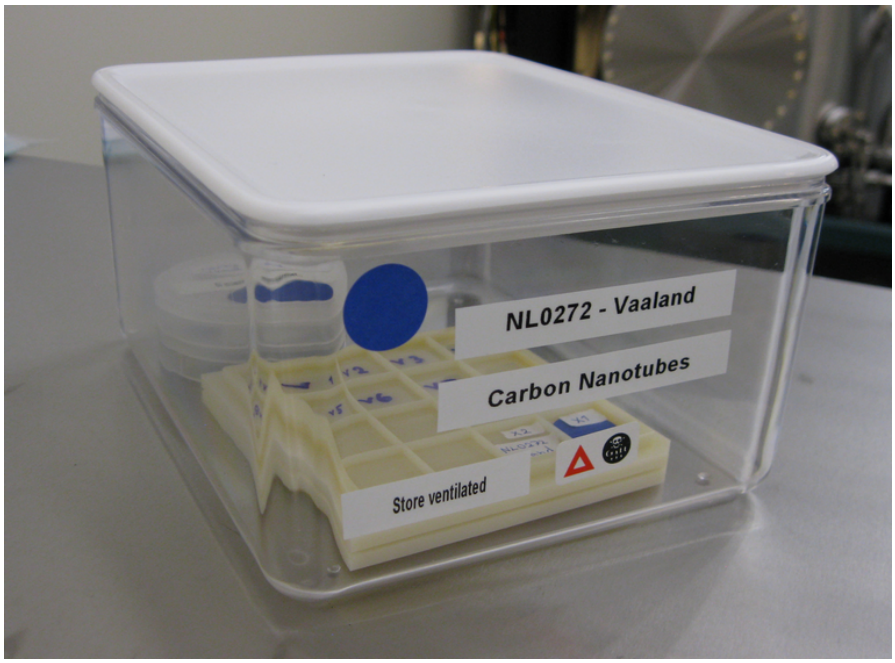

FIGURE E.1: Photograph of storage box used to store samples.