Carbon based materials for MEMS applications

Tan, Chong Wei

2009

Tan, C. W. (2009). Carbon based materials for MEMS applications. Master's thesis,
Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/15557>

<https://doi.org/10.32657/10356/15557>

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TAN CHONG WEI

2009

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CARBON BASED MATERIALS FOR MEMS
APPLICATIONS**

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**SCHOOL OF MECHANICAL & AEROSPACE
ENGINEERING**

2009

CARBON BASED MATERIALS FOR MEMS APPLICATIONS

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Master of Engineering

2009

Acknowledgments

I would like to express my honest admiration to my supervisor, A/Prof Miao Jianmin and Prof Tay Beng Kang, who has helped me greatly during my two years of study in NTU. His innovative and thoughtful ideas related with MEMS fabrication have helped me a lot in my project and his cheerful and friendly demeanor has increased the level of comfort.

I would like to extend my thanks to my lab mates Dr Chen Xiaofeng, Pradeep, Tan Chee Wee, Nay Lin, Xu Ting, for sharing their experiences and provided me with much help.

Thanks are also due to the technicians of the MMC lab, Mr. Pek Soo Siong for the sputtering and e-beam deposition processes, Mr. Wong Kim Chong for oxidation and Mr. Nordin Bin Abdul Kassim for SEM characterization.

Thanks are also given to Mr Liu Kai Yu for the support for the growth of Si_3N_4 and SiO_2 in micro fabrication laboratory in school of EEE.

I would also thank my family for their encouragement and support. I am grateful to all of my friends in NTU, especially Edwin and Dunlin for their help and guidance.

Finally I thank NTU for giving me a chance to study here.

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Abstract

CNTs have been a subject of interest by many researchers since its discovery by Ijima in 1991. With its excellent electrical and mechanical properties, many researchers have exploited its advantageous electrical properties for use in integrated circuits interconnects and field emission devices. However, very few researchers have explored its extraordinary mechanical properties. With its high elastic modulus and high buck resistance, CNTs would make very good structural materials.

Many researchers have been trying to control the density of the CNTs growth by using sophisticated and expensive techniques such as electron beam lithography and ion beam bombardment. Density control of CNTs has been demonstrated by a cheap novel combination of steps consisting of annealing, etching and ultraviolet overexposure. Sub-micron sized single CNT has been successfully demonstrated using the above-mentioned technique.

Two different and completely new methods of utilizing CNTs are being introduced, namely as templates and damping. It has been demonstrated that materials can be deposited and encapsulate the CNTs pillars. The ‘nanoballs’ effect of top layer material on CNTs has also been explained. Successful coverage on single CNT has been demonstrated. The possibility of using DLC-CNTs hybrid material has been successfully shown.

Chapter 1: Introduction

1.1 Carbon Based Materials

Carbon is essential to all known living systems. Without it, life will not exist as the way we know. Carbon occurs in all organic life and is the basis of organic chemistry. When bonded with oxygen, carbon forms carbon dioxide, which is the main carbon source for plant growth. When united with hydrogen, it forms various flammable compounds called hydrocarbons which are essential to industry in the form of fossil fuels. It is the major economic use of carbon that is not defined in terms of living or formerly-living material (such as food and wood).

Crude oil is used by the petrochemical industry to produce useful products for example, petrol, diesel, liquified petroleum gas (LPG), kerosene, etc, through a distillation process in refineries. Carbon-containing polymers, often with oxygen and nitrogen ions included at regular intervals in the main polymer chain, form the basis of nearly all-industrial commercial plastics.

As the free element, it forms allotropes from different kinds of carbon-carbon bonds. A few examples of them are shown in Figure 1 below.

Figure 1: Different Allotropes of Carbon

Carbon is able to bond with carbon or it can also form chains with a wide variety of other elements, forming nearly ten million known compounds.

Recently discovered nanostructured forms called fullerenes include buckyballs such as C_{60} , nanotubes, and nanofibers. Because of their high strength-to-weight ratio, it is hoped that many of these carbon compounds will soon be practical for use in advanced structural composite materials.

This bring us to two particular popular materials that are being introduced here, namely Carbon Nanotubes (CNTs) and Diamond Liked Carbon (DLC).

1.1.1 Carbon Nanotubes (CNTs)

The physics of carbon nanotubes has rapidly evolved into a research field since their discovery by Iijima [1] in multiwall form in 1991 and as single walled tubes two years later.

CNTs have remarkable properties such as ballistic electron transport and large elastic moduli. The high surface area and chemical inertness of nanotubes grown directly onto desired substrates makes them attractive for demanding applications such as electrochemistry, electrodes for fuel cells and super capacitors [2-7].

CNTs are commonly deposited by arc discharge, laser ablation and chemical vapor deposition. In the past few years, the growth techniques employed have progressed greatly. In particular, large effort has been put into producing single-wall carbon nanotubes (SWCNTs). This particular kind of nanotube has only one cylindrical wall and therefore naturally is a nanometer-sized material suitable for electronic applications [8,9]. Significantly, the way the single layer of graphene wraps around itself determines whether the nanotube will behave as a semiconductor or a metal [10].

MWNTs can be deposited by using the plasma enhanced chemical vapor deposition (PECVD) methods onto substrates coated with a suitable transition metal catalyst [11–17]. The essential parameters involved in the growth of vertically aligned carbon nanotubes (VACNTs) are the feed gas, the nature of the catalyst, and the substrate temperature [18].

1.1.2 Diamond-Like Carbon (DLC)

Diamond like carbon (DLC) film has been well known for its high hardness [19], good thermal conductivity [20], low friction coefficient [21], chemical inertness [22], and transparency over wide wavelength region particularly infrared [23], and excellent wear resistance [24].

The most attractive feature of DLC is that they can be grown at relatively low temperature on varieties of substrates and the extent to which the properties can be tuned in contrast to the diamond deposition techniques requiring high temperature. This makes DLC an important technological material.

DLC for silicon-based MEMS can be deposited at low temperatures using various techniques namely: filtered cathodic vacuum arc (FCVA) [25,26], pulsed laser deposition (PLD) [27], plasma-enhanced chemical vapor deposition (PECVD) [28], ion beam deposition [29,30], magnetron sputtering [31,32] and microwave assisted CVD [18-19]. DLC deposited by the FCVA technique [25,33] and magnetron sputtering on silicon [33,34] can be patterned by lift-off followed by anisotropic wet etching using KOH or tetra methyl ammonium hydroxide (TMAH). However, high compressive stress of up to 9 GPa is often found in DLC deposited by FCVA, which is a big challenge for the fabrication of MEMS, e.g. resonators [33].

The common feature relevant to these techniques is that the property of the deposited DLC film is governed by the energy of the impinging hydrocarbon ion species on the substrates. The negative bias voltage applied

to the substrate during growth dictates the ion energy and hence the film properties.

1.2 Applications of Carbon Based Materials for MEMS

Carbon based materials are ideally suitable as molecular level building blocks for nanoscale systems design, fabrication, and applications. From a structural or functional materials perspective, carbon is the only element that exists in a variety of shapes and forms with varying physical and chemical properties.

The current generation of MEMS devices is fabricated using processing technology derived from silicon microelectronics. Although silicon is suitable for many applications, its low toughness, low creep strength, high wear rate and high friction coefficient limit its use in the more demanding applications of MEMS. There is a strong drive to make MEMS from higher performance materials, such as biocompatible carbon-based materials. Diamond-like carbon coated MEMS microstructures like proof-masses, freestanding membranes, crosses and beams, carbon based beam cantilevers and freestanding micro bridges have been produced and manufactured.

One exciting area is the integration of nanotechnology, especially carbon nanotubes with carbon based MEMS devices, with potential applications such as optoelectronics mirrors, micro-sensors and actuator devices.

1.2.1 Applications of CNTs in MEMS

CNTs have been commonly used in microelectronics due to its ballistic transport of electrons and the extremely high thermal conductivity along the tube axis [35]. Metallic CNTs show ballistic conductivity at room temperature [36] enabling CNTs to carry very high currents ($> 10^9 \text{ A/cm}^2$) without electro migration failure [36]. Phonons also propagate easily along the nanotubes [36]. The measured thermal conductivity of an individual MWNT at room temperature is $> 3000 \text{ W/m}\cdot\text{K}$ [37], which exceeds the conductivity of diamond ($2000 \text{ W/m}\cdot\text{K}$). Based on these advantageous properties of CNTs, researchers have reported the integration of CNTs into electrical interconnect applications [38-40].

CNTs based composites have been introduced to MEMS dielectrics due to their abilities to exhibit modifications in term of electrical and thermal conductivity [41,42] and also RF performances [43,44], depending on the CNT proportion.

Recently, CNTs have become excellent candidates for the design of nanoelectromechanical systems (NEMS) due to their extremely high directional stiffness[45], ability to accommodate very large mechanical strains [46], and depending on diameter and helicity, act as 1D metals or semiconductors [47]. Because of these unique properties, coupled with their low mass and chemical inertness, CNTs represent ideal materials for enabling many high-performance NEMS devices. Nanotube-based NEMS have been demonstrated already in applications involving nanotweezers [48], memory devices [49], and tunable oscillators [50]. Nano-relays [51,52]

are another promising application of nanotubes that offer the potential for high-performance switching, with high-speed operation at low actuation voltages and power.

1.2.2 Applications of DLC in MEMS

MEMS offer great potential for integrating sensors, actuators, and electronics in a miniature package. Their functionality combined with their size represents a significant technological advancement. However, this small size is the root of engineering difficulties.

Applications of DLC films in MEMS are mainly split into two categories: surface coatings and structural materials. Due to the small motive forces that MEMS produce, friction becomes an important concern. Another problem with frictional forces is that they often accelerate wear. The gaps between MEMS components are often in the order of microns. Due to these small dimensions, wear debris can cause jamming. Most MEMS are fabricated out of polysilicon due to the ease of batch processing in the semiconductor industry. Unfortunately, polysilicon on polysilicon contacts have poor friction and wear properties [53–57]. One method to alleviate the problems of stiction, friction and wear is to coat the MEMS device with a protective material. DLC has been proven to be able to provide a conformal coating that was found to greatly improve performance over uncoated devices [58]. Stiction occurs in MEMS devices when two or more bodies come into contact with one another and the separation force that is required is larger than the force that can be generated by the device [59,60]. At micron size,

the ratio of surface area to volume is large hence surface forces dominates. During the drying phase of the release process, capillary forces can cause stiction. Van der Waals or electrostatic forces during operational contact can also cause stiction to dominate and cease MEMS operation [61,62]. Thin DLC layers have been commonly used as coatings to improve the wear and friction of micro-components and to reduce stiction between microstructures and their substrates.

The high values of the elastic modulus of diamond and DLC have been exploited in the design of high frequency resonators and comb-drives for communication and sensing applications. Chemically modified surfaces and structures of DLC films have both been utilized as sensor materials for sensing traces of gases, to detect bio-molecules for biological research and disease diagnosis.

1.3 Present Status of Carbon Based Materials for MEMS

1.3.1 CNTs for Porous Layer Fabrication

MEMS are often being implemented in electronics applications hence there is a future need for nano patterning. The common techniques used in the fabrication of nanometer-sized functional devices are electron or x-ray beams lithography which are very expensive. Another disadvantage is the limit area that can be patterned at one time.

Akihiko Oide [63] has used anodic porous alumina as porous layer template. The proposed idea uses the method involving anodizing sputtered aluminum on silicon substrate. The structure produced is closely packed hexagonal holes.

At present, no researchers have used CNTs to produce porous layers on silicon substrate. Currently, there are only a couple of researchers who have used CNTs as flow tube in membrane [64,65]. That would require the CNTs to be of good quality and single walled in order for the flow to be smooth. It is almost impossible to remove the CNTs grown after the membrane layer.

1.3.2 CNTs as Stress Relief Layer for Tetrahedral Amorphous Carbon (ta-C)

Under the increasing demands in reliability, for example, mechanical loading, fracture strength has become an important attribute for MEMS devices. In a comparative study, three emerging MEMS materials have been considered: silicon carbide by atmospheric pressure chemical vapor phase deposition, ultra nano crystalline diamond (UNCD) by microwave plasma-enhanced chemical vapor deposition and tetrahedral amorphous carbon (ta-C) by pulsed laser deposition [66].

Among these ta-C exhibited the highest fracture toughness. Unfortunately, although ta-C can be deposited at room temperature, an annealing step at 600– 650 °C is necessary for residual stress relief hence restricting its application. Alternatively, hydrogenated amorphous carbon (a-C:H) may be

considered which is typically fabricated at low temperatures without high temperature annealing using plasma-enhanced chemical vapor deposition. However, a-C:H exhibited a much lower fracture strength of 0.82–1.36 GPa [66].

At the moment, no researchers have used CNTs as a stress layer for ta-C. This would prove to be a new area for exploration of new ideas.

1.4 Project Inspirations

In the recent years, there is great progress in the growth of CNT but it remains a challenge to grow CNT of good quality. The dependency on the quality of the CNT should thus be reduced to increase the cost efficiency for future developments.

In order to work towards the goal of achieving density controlled CNT growth, the first step taken is to identify the CNT that can be grown by varying different conditions such as different catalyst thickness, different etching time, different growth pressure and different deposition time. Nickel catalyst has been used for all the experiments conducted.

The template method is much better than the current method, e.g. nano imprint and etching. These two methods are not able to achieve high aspect ratio due to the limitations of the structure rigidity for nano imprint and mass transport for etching. Besides, nano imprint is only valid for polymer and not materials like silicon nitride and silicon oxide, which is very useful in semiconductors industry as insulators. The

smallest size attained so far with etching method is approximately $1\text{ }\mu\text{m}$ whereas the usage of CNT as template can bring the feature size down the tens of nanometer.

There have been also usage of focused ion beam and e-beam writing facilities to obtain nano sized holes but all these are limited to only hundreds of nanometer thick layer and hole feature size of minimum 100 nm . This will also means that the structural rigidity is also greatly reduced as compared to a $1\text{ }\mu\text{m}$ thick porous layer that the author is trying to achieve.

(a) Columns grown on Si (b) Layer grown (c) Columns removed

Figure 2: Creating Porous Template

A general overview of the process can be seen in Figure 2 above. Columns are first placed on a substrate. Following that, the selected materials for the porous layers are deposited and finally, the columns are removed and the pores are created.

Carbon nanotubes (CNT) with diameter in the range of nanometers will prove to be good material for the columns used in creating of the template for nano-porous layers.

The hardest, strongest, and slickest is such a mixture, known as tetrahedral amorphous carbon, or ta-C. For example a coating of only $2\text{ }\mu\text{m}$ thickness of ta-C increases the resistance of stainless steel against abrasive wear thereby changing its

lifetime in such service from one week to eighty five years. Such ta-C can be considered to be the "pure" form of DLC, since it consists only of sp^3 bonded carbon atoms. Fillers such as hydrogen, graphitic sp^2 carbon, and metals are used in the other six forms to reduce production expenses, but at the cost of decreasing the service lifetimes of the articles being coated. The various forms of DLC can be applied to almost any material that is compatible with a vacuum environment.

The main problem of ta-C is due to the high stress involved during deposition. Annealing can solve this problem, but a lot of modern electronics and devices cannot undergo these high temperatures. By exploiting the elastic properties of CNTs, it is possible to use the CNT pillars to reduce stress in thick ta-C films, hence retaining the strength of ta-C yet flexible film that can be used for damping or strengthening of materials as shown in figure 3 below. This serves as a breakthrough in the creation of a hard yet soft hybrid material.

Figure 3: Ultra Thick ta-C on CNTs

1.5 Objectives

The goal of this project is to create porous thin film layer with controllable varying pores size. This project is divided into various components and follows a systematic study that will eventually lead to the synthesis of porous thin film layer. The process flow in which the investigations are carried out is as follows:

- Carbon Nanotube (CNT) Growth on the PECVD equipment.
 - o Determine the effect of the catalyst thickness on the diameter of the CNT.
 - o Determine the effects of etching time on the CNT growth.
 - o Determine the effects of different deposition time.
 - o Determine the effects of different deposition pressure.
 - o Determine the effects of annealing time on nickel catalyst.

- Density control by using of lithography process
 - o Lithography by using standard MEMS lithography process.
 - o Lithography by using e-beam writer.

- Deposition of the thin films on the CNTs
 - o Deposition of silicon nitride (Si_3N_4)
 - o Deposition of silicon oxide (SiO_2)
 - o Deposition of nickel (Ni)

- Deposition of DLC
- Characterization of deposited thin films on CNTs
- Deposition of ultra thick ta-C using the CNT as stress relieved layer
- Characterization of ta-C layer

1.6 Organization of Report

The report is structured as follows:

- Chapter 2 presents the fundamentals of CNTs, DLC and MEMS fabrication technologies. Literature reviews are done on the growth mechanism of CNTs, current and potential applications of CNTs, structures and properties of DLC films and its potential applications. Main micro fabrication techniques are also being summarized.
- Chapter 3 presents the density control of CNTs growth. Influence of deposition temperature, pressure, time, acetylene flow rate, nickel catalyst thickness, ammonia plasma treatment and pre-annealing are being examined. Nickel catalyst patterning using a novel method is also being introduced here.
- Chapter 4 describes the deposition and growth of thin film layer on CNTs. SEM images of the deposited films are being shown and the relevant explanations given for the unusual effects of the ‘nanoballs’ Nickel has also being deposited on the CNTs tip which can be proposed for a future works. SEM results from the deposition of DLC on top of CNTs layer. Potential application of this new novel hybrid material is also being proposed.

- Chapter 5 gives a summary on the various experiments conducted followed by a general discussion and conclusion.
- Chapter 6 presents the recommendations for future work and development for the findings.

Chapter 2: Literature Review

2.1 Carbon Nanotubes (CNTs)

Carbon Nanotubes (CNTs) research was greatly stimulated by Iijima's findings in 1991. The initial observation of carbon tubules looks like elongated fullerenes in nanometer dimension. Ever since these early reports on the conditions for the synthesis of large quantities of nanotubes [67, 68], a lot of work has been done. Carbon nanotubes basically behave like rolled up cylinders of graphene sheets of sp^2 bonded carbon atoms, except that the tubule diameters in some cases are small enough to exhibit the effects of one-dimensional periodicity.

2.1.1 Structures of CNTs

A single-walled nanotube (SWNT) is made of a single graphite layer rolled up into a hollow cylinder whereas a multi-walled nanotube (MWNT) comprises of several concentrically arranged cylinders. The body of the cylinder is mainly made of hexagonal rings of carbon atoms with the ends capped by half dome-shaped half-fullerene molecules. The natural curvature in the sidewalls is due to the rolling of the sheet into the tubular structure, whereas the curvature in the end caps can be due to the presence of topological defects (pentagonal rings) or hexagonal rings depending on the structure. Figure 4 below show the drawings of two nanotubes, which can be capped in the zigzag and armchair structure.

(a) Zigzag (9, 0) structure

(b) Armchair (5, 5) structure

Figure 4: Drawings of Two Nanotubes Capped by Half C_{60}

It is convenient to specify a general carbon nanotube in terms of the tube diameter, d_t and the chiral angle, as shown in figure 5 below.

Figure 5: Four Different Graphene-Lattice Points

Fundamental Parameters and Relations

Some of the common equations used to define SWNT are shown in Table 1 below. The chiral vector C_h is defined in terms of integers (n, m) and the basis vectors a_1 and a_2 of the honeycomb lattice. The integers (n, m) uniquely determine d_t and θ . The length L of the chiral vector, C_h is directly related to the tube diameter d_t .

Chiral Vector	$C_h = na_1 + ma_2 \equiv (n, m)$
Unit Vectors	$a_1 = \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix} a$ $a_2 = \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} a$
Circumference of CNT	$L = C_h = a\sqrt{n^2 + m^2 + nm}$
Diameter of CNT	$d_t = \frac{L}{\pi} = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi}$
Chiral Angle	$\sin \theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}} \quad 0 \leq \theta \leq 30^\circ$ $\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$ $\tan \theta = \frac{\sqrt{3}m}{2n + m}$

Table 1: Fundamental Equations

Nanotubes of type (n, m) , as shown in Figure 6a below, are commonly called armchair nanotubes because of the $\backslash/\backslash/$ shape, perpendicular to the tube axis, and have a symmetry along the axis with a short unit cell (0.25 nm) that can be repeated to make the entire section of a long nanotube. Another type of nanotube $(n, 0)$ is known as zigzag nanotube (Figure 6b) because of the $\backslash\backslash$ shape perpendicular to the axis and as well as the short unit cell (0.43 nm) along the axis [69]. In addition, a large number of chiral nanotubes can be formed for $0 < \theta < 30^\circ$, with a screw axis along the tube axis and with a variety of hemispherical caps as shown in Figure 6(c).

Figure 6: (a) $\theta = 30^\circ$ (b) $\theta = 0^\circ$ (c) $0^\circ < \theta < 30^\circ$

The symmetry groups for carbon nanotubes can be either symmorphic {such as armchair (n, m) and zigzag $(n, 0)$ }, where the translational and rotational symmetry operations can be executed independently. On the other hand, the symmetry group can be non-

symmmorphic where the basic symmetry operations require both a rotation, and a translation, define by the equation 1 [70] shown below.

$$R = (\psi | \tau) \dots\dots(1)$$

Multiwall CNTs and Arrays

Most of the experimental observations on carbon nanotubes are multi-walled [71-73]. This has inspired a number of theoretical calculations to extend the theoretical results initially obtained for single-walled nanotubes to observations in multilayer nanotubes. These calculations for multi-walled nanotubes have been informative for the interpretation of experiments and influential for suggesting new research directions. The multi-wall calculations have been predominantly done for double-wall nanotubes, although some calculations have been done for four-walled nanotubes and some for nanotube arrays [72, 73].

2.1.2 Properties of CNTs

CNTs have been well known for some of its superior properties as compared to other materials. Listed below are some of the unique properties that are of interest, particularly its elastic properties that determines its feasibility as a stress relief layer for DLC.

Electronic Properties

The single and multi-wall nanotubes are interesting nanoscale materials for several reasons; A single-wall nanotube can be either metallic or a semi conducting depending on its chiral vector (n, m). A metallic nanotube is obtained when the difference between n and m is a multiple of three whereas if the difference is not a multiple of three, it is semi-conducting. In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper.

CNTs possess an intrinsic superconductivity and behave as thermal conductors and field emitters. The energy band gap of the CNTs is related to the diameter and helicity of the tubes. The larger the diameter of CNTs, the lower the energy gap will be. Generally, CNTs comes in three types: large energy gap, tiny energy gap and zero energy gaps, leading to different current densities. MWCNTs have been able to withstand high current density from 10^6 to 2.4×10^8 A/cm² without any deterioration due to the ballistic type of electron transport, without any resistance and scattering. This ballistic behavior is due to the one-dimensional electronic structure of the CNTs.

Mechanical Properties

Carbon nanotubes are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 GPa. Since CNTs have a low density for a solid of 1.3-1.4 g/cm³, its specific strength of up to 48,462 kN·m/kg is the best of known materials, compared to high-carbon steel's 154 kN·m/kg [74].

Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5 % and can increase the maximum strain the tube undergoes before fracture by releasing strain energy.

CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsion or bending stress.

Thermal Properties

CNTs have shown extraordinary heat capacity and thermal conductivity. It was predicted that CNTs have similar thermal properties at room and elevated temperatures but unusual behavior

appears at low temperatures due to the effect of phonon quantization. The mechanical and thermal properties of CNTs have not yet been measured, mainly because of the difficulties of obtaining pure homogeneous and uniform samples of tubes. However, it has been shown that the thermal conductivity of an individual MWCNT is 6000 W/mK measured at room temperature that is three times higher than that of diamond and graphite [75]. At room temperature, thermal conductivity of SWCNT can reach values between 1750-5800 W/mK, which is higher than graphite [76].

Thermal conductivity is one-dimensional for CNTs like electrical conductivity. Theoretical calculations and experimental measurements shows the thermal conductivity for SWCNTs at room temperature could vary between 1800 and 6000 W/mK [77, 78] and for MWCNTs, more than 3000 W/mK was confirmed from the measurement of a single MWCNT [79].

Chemical Properties

CNTs are sensitive to chemical and environmental interactions due to its small radius, large specific surfaces and π - π rehybridization. The chemical properties of interest include opening, wetting, filling, absorption, charge transfer, doping etc. CNTs reactivity is directly related to the π -orbital mismatch caused by an increased curvature.

A smaller CNT diameter results in increased reactivity and vice-versa.

Optical Properties

Defect free SWCNTs offer direct band gap, well-defined band and sub-band structure, which is ideal for optical and opto-electronic applications. Previous studies revealed that the electronically induced optical emission [80] and photoconductivity [81] for individual SWCNT. Electrical control of the light emission of individual SWCNT allows detailed characterization of the optical properties.

Magnetic Properties

The magnetic properties are studied with electron spin resonance (ESR), which is useful for understanding the electronic properties of graphite. Magnetic properties such as anisotropic g-factor and susceptibility of CNTs are expected to be similar to those for graphite while some unusual properties may exist for CNTs. It was also found from the ESR studies of Pauli behavior that the aligned MWCNTs are either metallic or semi-metallic [82].

Wetting Properties

CNTs are generally hydrophobic in nature and do not show wetting behavior for most aqueous solvents. Surface tension is the main factor deciding the wetting characteristics of CNTs with metal surfaces. Liquids with low surface tension will only wet the CNT surface [83].

2.1.3 Growth Mechanism of Carbon Nanotubes

The structural and electronic properties are directly related to the atomic structure of the tube. Hence it is essential to understand what controls the nanotube size, the number of shells, the helicity, and the structure during synthesis. The growth mechanism for chemical vapor deposition (CVD) follows a sequence of steps, which are discussed below:

1. Diffusion of precursor through a thin boundary layer to the substrate.
2. Adsorption of species onto the surface of catalyst.
3. Surface reactions leading to film growth.
4. Desorption of product species.
5. Extrusion and elongation of CNTs.

There are two ways to grow carbon nanotubes as shown in Figure 7 below.

Figure 7. Schematic diagram of Root growth and Tip growth mechanism [84]

For root growth mechanism, nucleation of CNTs takes place at high temperature. CNT is formed by the process of extrusion and grows upright while the catalyst particles remain attached to the substrate. The size of CNTs growth depends on the size of the metal catalyst particle. Precursor gases such as ethylene and acetylene decompose into carbon and hydrogen. The carbon atoms diffuse around or in the metal particles and start growing in the form of cylindrical tubes on the surface of a metal catalyst particle [85-87]. Figure 8a and b below shows the CNTs grown by root growth mechanism.

(a) Magnified SEM image showing metal nanoparticles at the base ends of CNTs

(b) low magnified HRTEM image of base ends of CNTs [87]

Figure 8: Base Growth Images

For tip growth mechanism, it is assumed that the metal catalyst particles are either floating or supported by graphite and are spherical or pear-shaped. The deposition takes place on only one half of the surface. Carbon atoms diffuse along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter, thus forming a cylindrical closed kind of tube [84]. Figure 9a and 9b below shows the CNTs grown by tip growth mechanism.

(a) TEM image of nanotubes showing Ni on top surface

(b) Shape of Bottom Tubules [84]

Figure 9: Images of Tip Growth

2.1.4 Synthesis of CNTs

The earliest approach to produce nanotubes was the arc process [1] as pioneered by Iijima. Following behind was the laser ablation technique developed at Rice University [84]. Recently, chemical vapor deposition (CVD) has become a common technique to grow nanotubes. The advantages

of all these techniques depend on the type of applications. For example, development of composites and other structural applications may requires the ability for speedy production whereas for applications in nanoelectronics, field emission, displays and sensors, the ability to achieve controlled growth is of importance. Regardless of the applications and growth approach, the ability to control the diameter and chirality of the nanotubes is critical to realize the promise of carbon nanotubes.

There are several methods for catalyst preparation that can be used for CNT growth. One such method involves the use of solution-based catalysts. However, one common problem to this approach is the difficulty of confining the catalyst from the solutions to small patterns. In contrast, physical process such as sputtering and e-beam deposition can deal with small patterns and is also quick and simple in practice. There has also been the most recent advancement whereby gas catalyst is being used and CNT can be grown on substrate without pre-deposited catalyst or even grown without substrate.

There are three main methods used to produce CNTs and they are being discussed below:

Laser Ablation

Figure 10: Schematic Diagram of Laser Ablation Apparatus

The apparatus shown in Figure 10 above consists of an oven maintained at a temperature of 1200 °C. The oven consists of a graphite target, which is vaporized by the emission of a pulsed or continuous laser. In order to maintain the pressure and inert atmosphere inside, inert gases such as helium or argon are being introduced in. Due to vaporization, very hot vapor clouds will form and cool rapidly leading to the formation of small carbon molecules. These atoms will then condense to form large clusters along the formation of fullerenes. The catalyst then condenses and attaches to the carbon clusters. Single walled nanotubes (SWNTs) will be formed from these initial clusters. The size of catalyst particles increases until no more carbon can diffuse through the catalyst particles. Multi walled nanotubes (MWNTs) are formed when Van der Waals forces hold and bundle the single walled nanotubes together [85].

Electric-Arc Discharge

Figure 11: Schematic Diagram of Electric-Arc Discharge Apparatus

Nanotubes are formed through the arc vaporization of two carbon electrodes placed in a confined space filled with inert gas, like helium or argon at low pressures. One of the carbon rods vaporizes due to the discharge and a small rod shaped deposit is formed on the other rod [1]. Single walled nanotubes or multi walled nanotubes can be grown using the method shown in Figure 11 above. The carbon nanotubes are separated from the catalyst metal and soot.

Chemical Vapor Deposition

This method involves heating of a catalyst material to a high temperature in a tube furnace and allowing the flow of hydrocarbon gas through the tube reactor for a specified period. Catalyst layer is prepared by depositing a thin layer of transition metal on the substrate using sputtering process. Special surface treatment methods such as chemical etching or thermal annealing are

applied to induce catalyst nucleation. Thermal annealing results in cluster formation on the substrate around which CNTs will grow.

Thermal Chemical Vapor Deposition (Thermal CVD)

Figure 12: Photo of Thermal CVD system

Figure 13 Schematic Diagram of Thermal CVD Apparatus [86]

Figure 12 shows a photo of the thermal CVD equipment used in Micro Machines Center and Figure 13 above shows the schematic diagram of thermal CVD apparatus. Chemical Vapor Deposition is the heterogeneous decomposition of gaseous reactants by the thermal energy of the substrate and subsequent deposition of a solid on the surface of the substrate. One

main advantage of this method lies in the simplicity of design and it is possible to expand the equipment for mass production purposes. For CNT growth, a catalyst provides the mechanism for carbon absorption and CNT growth. A metallic catalyst, such as iron, nickel, or cobalt, is deposited onto a substrate. The sample is placed in a furnace and heated to a temperature between 700 to 1000 °C. The reacting gases such as argon (Ar), hydrogen (H₂) and acetylene (C₂H₂), called precursors, are introduced into the chamber where they are decomposed primarily at the catalyst particles by thermal energy. The carbon is absorbed into the catalyst and forms a solid solution with the metal. When the catalyst becomes supersaturated, the carbon precipitates out as a CNT. Single and multiple walled CNT have been grown using thermal CVD. The iron layer forms nanoparticles in the pores of the silicon, which interact strongly with the substrate and remain on the surface during growth. CNT growth is further enhanced by the ability of the precursor gas to permeate into the pores of the silicon that do not contain an iron nanoparticle and to diffuse into the catalyst from the sub-surface level, thereby effectively increasing the catalyst absorption area and boosting the growth rate. CNT grown by thermal CVD have been shown to exhibit a base growth mechanism, in which the catalyst particle remains on the surface while the closed end of the CNT increases in length. The carbon is precipitated out of the top of the catalyst particle in a continuous manner, as more carbon is diffused into the catalyst to replace the carbon that formed the CNT. Growth ceases when carbon is no longer supplied to the catalyst.

Figure 14a and 14b below shows SEM images of the substrate before and after CNTs growth respectively.

(a) Before CNTs Growth

(b) After CNTs Growth

Figure 14: Patterned Iron Catalyst before and after CNT growth using Thermal CVD

Plasma Enhanced Chemical Vapor Deposition (PECVD)

Figure 15: Photo of the PECVD equipment

Figure 16: Schematic Diagram of PECVD System

Plasma enhanced chemical vapor deposition (PECVD) has been investigated extensively recently by researchers due to its ability to produce aligned CNT. Figure 15 above shows a photo of the PECVD equipment used for the project and Figure 16 shows the schematic diagram of the PECVD system. The PECVD first emerged in use because certain processes cannot tolerate the high wafer temperature of the thermal CVD. The low temperature operation is possible because the high-energy electrons in the plasma enable the precursor dissociation. For CNT, the precursor dissociation occurs at the surface of catalyst particles producing carbon needed for CNT growth. The true role of plasma in CNT growth is still not clear although there is evidence that the electric field in the plasma enables more vertically aligned CNT than compared to thermal CVD.

The eventual particle size and resultant CNT diameter seem to correlate to catalyst film thickness. Thinner films will more likely lead to smaller particles and nanotube diameters.

The process of plasma enhanced chemical vapor deposition is similar to that of thermal CVD. A cleaned substrate (usually silicon or glass) is coated with a metal that has been shown to act as a catalyst for CNT growth, such as Ni, Fe, Co, etc., using various deposition methods (e-beam evaporation, sputtering, etc.). The coated samples are placed into the PECVD reactor, which is then pumped down to a low base pressure (~ 2 mbar). The carbon containing and reacting gasses are introduced into the chamber through a network of mass flow controllers to regulate the flow rate and gas composition of the mixture. The high voltage causes an ionization avalanche resulting in plasma formation, which acts to decompose the gas into its components. The exact growth mechanism of CNT formation is not exactly known, however it is believed that carbon enters into the catalyst until it is supersaturated. Finally, the carbon is precipitated out of the catalyst in the form of a CNT. This method has more variables than the other techniques and allows for independent control of growth parameters. It has been shown that substrate temperature, catalyst thickness, chamber pressure, precursor flow rate, gas ratio, order of gas introduction, applied high voltage and current, and electric field orientation have effects on CNT growth rate, diameter, and alignment. Figure 17 and 18 below shows the SEM images of CNT grown using the PECVD equipment.

Figure 17: SEM Image of CNT Grown on Silicon Substrate

Figure 18: Close Up SEM image of CNTs Grown Using PECVD

2.1.5 Current and Potential Applications of CNTs

Production of Filtration and Nanoporous Layer Using CNTs

Bulk micro machined nanofilter

Figure 19: Bulk Micro Machines Nanofilter

The proposed silicon nanofilter consists of two bonded silicon wafers: the micro machined filtration structural wafer and the cap wafer as shown in Figure 19 above. Fluids enter through the hole etched in the cap wafer, then flow horizontally through the filtration channel as defined by the gap between the cap wafer and the machined features on the structural wafer, and then out the hole etched in the structural wafer. [87]

Development and characterization of on-chip biopolymer membranes

Figure 20: On-chip Biopolymer Membranes

Figure 20 above shows the steps involved for the manufacturing of the on-chip biopolymer membranes. Single side polished silicon wafers were cleaned and coated on both sides with 200 nm of low-stress silicon nitride using low-pressure chemical vapor deposition. A two dimensional array of $1\text{ mm} \times 1\text{ mm}$ squares was patterned on the backside of the wafer (unpolished) using standard photolithography techniques, and the silicon nitride layer was etched using reactive ion etching. A pattern from the second mask containing arrays ranging in size from $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ to $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$ squares was aligned on the top with the previously patterned regions on the unpolished side (bottom), and the interstitial layer of silicon was removed by etching in KOH.

The resulting substrate consisted of a silicon wafer with a 200 nm thick porous silicon nitride layer suspended across 1 mm^2 holes etched completely through the wafer. The suspended nitride layer had the $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ to $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$ openings for filtration; Membranes were cast directly onto the silicon wafers from cellulose acetate (CA) solutions by spinning the polymer solution onto the wafers. Polymer solutions were prepared by dissolving CA (39.8 wt% acetyl content, MW= 30,000), in *N,N* - dimethylacetamide (DMAc), at various concentrations. Spinning times varied from 5 to 30 seconds. After spinning, the coated wafers were immersed in a water bath for 10 minutes at variable temperatures, removed and air dried. SEM images showed that the resulting membranes had a thin porous skin, which was few nanometers thick, and large voids, up to several micrometers in width and depth, in the interior [88].

Carbon Nanotube-Embedded Silicon Nitride Membrane [89]

Figure 21: Process Steps for Carbon Nanotube-Embedded Silicon Nitride Membrane

The entire fabrication process for these membranes is illustrated in Figure 21 above. In addition, the nanotubes can also serve as a template for the production of nanoporous silicon nitride since they can be selectively removed by oxidation. The other advantage of silicon nitride is its vapor phase deposition. Materials deposited in the liquid-phase such as spun-on polymers require elaborate curing processes to reduce CNT agglomeration and ensure retention of alignment. The crucial step in the process that enables membrane fabrication is filling the voids between the nanotubes with a rigid, impermeable material that conforms to the tubes. The properties of low-stress silicon nitride render this material particularly

suitable for this purpose. Thus, after tube growth, the samples are placed into a low-pressure CVD furnace to deposit a low-stress silicon nitride layer, using a deposition temperature of 800 °C and a 6:1 ratio of dichlorosilane to ammonia. A target film thickness between 400 and 800 nm was found sufficient to fill the bulk of the 5-10 μm thick nanotube forest and encapsulate the top. The result of the process is shown below in Figure 22.

Figure 22: SEM Images of Holes in Membrane and CNT Growth [89]

The possible applications of carbon nanotubes arise from their remarkable properties such as the high Young's modulus, high thermal conductivity, ballistic electron transport and high aspect ratio structure. Some of the application areas of CNTs include nanoelectronics [90-92], quantum wire interconnect technology [92, 93], field emission devices [94, 95], composites [96], flow sensors [97], pressure sensors [98], gas detectors [99, 100], electromechanical actuator [101], chemical and biological sensors [102, 101] and scanning probe microscope [103-105].

Structural Reinforcement

CNTs have been used for two important classes of micro devices, namely electrostatic micro actuators and flexural-mode micro beam resonators. Electrostatic actuators are widely employed in MEMS for applications ranging from displays and micro-flow controllers to sensing and communications [106]. Engineering the structural stiffness and natural frequency of bending vibrations is of paramount importance since these parameters govern the actuation voltage, which can be as large as several hundred volts in commercial MEMS and the speed of actuation. It was shown that even within the current limitations on nanocomposite manufacturing technology; reinforcement with aligned carbon nanotubes is an excellent approach for tuning the stiffness and natural frequency of electrostatic micro actuators [107].

2.2 Diamond-Like Carbon (DLC)

Carbon being the sixth element in the periodic table has fascinated many people by the multiple forms that it can appear in. Diamond-like carbon (DLC) is an amorphous form of carbon with a large fraction of sp^3 bonds. There are several

ways to synthesize DLC. One of the first method used involved chemical vapor deposition from methane at low temperatures. The resulting DLC films contained a large fraction of hydrogen. It was believed that hydrogen is necessary to stabilize DLC and correlations between sp^3 fraction and hydrogen content were developed. However, in 1989, the formation of high quality DLC films by pulsed laser ablation of carbon clearly demonstrated that hydrogen is not necessary for the stability of sp^3 bonds. Thus, the concept of hydrogen free DLC was clearly established [108].

There are a great variety of structures and properties exhibited by carbon stems due to its unique chemistry. The ground state configuration of carbon is $2s^2 2p^1_x 2p^1_y$, which suggest that a carbon atom should be capable of forming only two bonds. The tetra valence of carbon is achieved by allowing for promotion (the excitation of an electron to an orbital of higher energy). The configuration, $2s^1 2p^1_x 2p^1_y 2p^1_z$, which has four unpaired electrons in separate orbital is formed by the promotion of a 2s electron to a 2p orbital. These electrons may pair with four electrons in orbital provided by four other atoms and hence form four electron pair bonds. The formation of four bonds is a characteristic feature of carbon because the promotion energy is quite small due to the repulsion relieving of electron-electron when the promoted electron leaves a doubly occupied 2s orbital and enters a vacant 2p orbital [109].

The concept of hybrid orbital is being discussed to have a more complete picture of the bond formation process with the promoted state of carbon. It is a common understanding that the electron density distribution in the excited atom is equivalent to the electron density in which each electron occupies a hybrid orbital formed by

the interference between the C 2s and C 2p orbital. The specific linear combinations that give rise to four equivalent hybrid orbitals are termed sp^3 hybrid orbital.

$$\left. \begin{aligned} h_1 &= s + p_x + p_y + p_z \\ h_2 &= s - p_x - p_y + p_z \\ h_3 &= s - p_x + p_y - p_z \\ h_4 &= s + p_x - p_y - p_z \end{aligned} \right\} \dots \dots \dots (2)$$

These four sp^3 orbitals can, for example, form four bonds with four H atoms to produce a CH_4 (methane) molecule.

Likewise, instead of using four orbitals to form hybrids, sp^2 hybrid orbitals can be formed by super positioning of an s orbital and two p orbitals.

$$\left. \begin{aligned} h_1 &= s + 2^{1/2} p_y \\ h_2 &= s + \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \\ h_3 &= s - \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \end{aligned} \right\} \dots \dots \dots (3)$$

which can form C_2H_4 (ethane) molecules, for example.

A similar description applies to the linear acetylene molecule $H-C \equiv C-H$, but now the C atoms are sp hybridized and the bonds are formed by using hybrid atomic orbitals of the same form.

$$\left. \begin{aligned} h_1 &= s + p_z \\ h_2 &= s - p_z \end{aligned} \right\} \dots \dots \dots (4)$$

The three types of hybridization are schematically illustrated in Figure 23 shown below.

Figure 23: Schematic illustration of the three possible hybridizations of carbon

[109]

In the case of diamond, all the carbon atoms form bonds with the four sp^3 hybrid orbitals whereas graphite uses the sp^2 hybridization to form a trigonal plane consisting of three bonds and the remaining p_z orbital to form a relatively weak bond that is perpendicular to the triangle. This configuration makes graphite a layered structure that can be used as a good lubricant. The great diversity of carbon properties arises from the differences in bonding state and atomic structure: creating one structure that is considered to be the hardest known material and its counterpart has been widely used as a good lubricant.

Hydrogenated DLC films were the most common in the past and the preparation methods were traditional vapor deposition processes that are thermodynamically close to equilibrium. The hydrogen is envisaged to affect adversely both stability and hardness of the DLC films.

2.2.1 Properties of DLC

Stresses in Thick DLC Films

The most serious problem that has plagued the fabrication and application of relatively thick high quality DLC films has been the internal compressive stress that is associated with highly fourfold method [110-112]. Internal stress as high as 10 Gpa has been widely reported, associated with highly tetrahedral DLC. This stress level will unavoidably lead to concerns about adhesion. Therefore methods to reduce or even eliminate the internal compressive stresses in DLC films have long been an important research field.

2.2.2 DLC Deposition

Ion Beam Deposition

There are two types of ion beam deposition. The first kind is the direct ion beam deposition where ion beam of controlled composition, energy and flux is directed onto a substrate. Figure 24 below shows a schematic illustration of the working principle. [113] The impacting ions in this technique are used to supply both the deposition atoms and the energy required for improved film formation. The very smooth nature of the deposited films is usually explained on the basis of surface energy. The total surface energy is equal to the product of surface tension and the surface area. The steps are shown below:

1		Impinging ion providing energy for lateral motion of surface atom into advantageous site.
2		Sputtering of impurity gas atom from surface
3		Sputtering of loosely bonded solid atom from surface
4		Solid atom or ion depositing on surface
5		Gas atom contaminating surface

Figure 24: Schematic of Direct Ion Beam Deposition [113]

The second type of ion beam deposition is the ion assisted deposition.

Figure 25 below shows the schematic illustration of the system:

Figure 25: Ion Assisted Deposition

In this technique, films can be produced at a much faster rate and over a larger area than with direct ion beam deposition because there is no need to produce ions of the material to be deposited. The non-equilibrium ion energy is provided by a gaseous ion source operated in parallel with the source of atoms or clusters of the material to be deposited [113]. This configuration still allows the deposition chamber to be maintained at a high vacuum permitting the retention of ion energy and minimizing substrate contaminations.

Cathodic Arc Deposition

The ion flux emitted from a cathodic arc is closely related to the composition of the target and is highly energetic and excited. This method has been reported as a suitable process for producing high wear resistant carbon films over a large area [114]. Using this technique, pure DLC films and doped DLC films can be processed easily [115, 116]. Figure 26 below shows a schematic view of the carbon deposition setup [114]. The cathodic arc is a low voltage high current discharge in which the current flows from

the cathode at one or more small cathode spots, 5-10 μm in diameter. The extremely high current densities at the cathode spot causes violent emission of the solid cathode material, which is subsequently ionized in the intense plasma, associated with the cathode spot. For a carbon cathode, the emitted material is primarily C^+ ions with kinetic energies characterized by a broad peak at about 22 eV [117]. Sufficient plasma is emitted to make the discharge self-sustaining in a vacuum and the cathodic arc is often referred to as a vacuum arc.

Figure 26: Cathodic Arc Deposition System

The major modification of the conventional cathodic arc evaporation technique is the filtered cathodic vacuum arc (FCVA) deposition technique. Figure 27 below shows the schematic configuration of the equipment:

Figure 27: Filtered Cathodic Vacuum Arc Deposition

During FCVA deposition, the neutrals and macroscopic particles are removed from the plasma streams hence only the charged species in the plasma reach the exit and are deposited onto the substrate. Films of DLC prepared using a FCVA are found to possess high hardness and density [118]. The high compressive stress (9-10 GPa) found in the DLC films made by FCVA indicates that the film quality is high and the sp^3 to sp^2 ratio usually scales with the internal compressive stress [115, 119, 120].

2.2.4 Current Applications and Associated Problems of DLC

Current commercialized application of DLC thin coatings includes microtribology in the microelectronics industry [121, 122]. Potential applications under exploration include flat panel displays, biomedical devices [123, 124] and electronics devices [125, 126].

Medical applications of DLC include surface engineering of replacement human body joints such as hip or knee joints. It is usually realized that the tribo-chemical conditions are very severe where even the best materials such as Co-Cr-Mo alloys that are used currently are dissolved or wear by at least 0.02-0.06 mm in 10 years. (Mean linear wear rate)

In order to achieve high wear resistance, hard and strong surfaces, thicker DLC will be preferred but the problems associated with thicker DLC is the high stress involved. So far, no other research groups have demonstrated the concept of using a hard on flexible material. The usage of DLC on CNTs is the first of its kind in the research path.

2.3 MEMS Fabrication Technologies

The initial development of MEMS technology was in the 1960's using fabrication facilities developed for VLSI technology. While the electronics were fabricated using integrated circuit (IC) process such as CMOS or BICMOS, the micro mechanical components were fabricated using compatible micromachining processes that selectively “machine” or etch away parts of the silicon wafer, or add new structural layers to form the mechanical and electromechanical devices [127].

The fabrication process to realize MEMS is a combination of conventional IC processes and specialized technologies, which are unique to silicon micromachining. Micromachining is the key to technology for the fabrication of solid-state MEMS devices such as micro actuators and micro sensors. The technologies concerned are bulk micromachining, surface micromachining and

micromoulding technologies, including classical electroplating, the HexSil [128] and the LIGA [129] process.

2.3.1 Bulk Micromachining

Bulk micromachining is a process whereby the silicon substrate is selectively removed to shape and form the desired micromechanical elements. It is in fact a subtractive process. Figure 28 below shows a typical bulk micromachined structure.

Figure 28: Bulk Micro Machines Structure

There are many fabrication methods of machining the silicon substrate. The typical methods include isotropic etching, anisotropic, electromechanical etching, spark milling, mechanical milling, ultrasonic milling, laser etching, plasma-phase or dry etching etc [130].

Bulk micromachining is essentially the formation of a desired microstructure via utilization of the bulk of the structure. This extension of definition includes the widespread use of wafer bonding technology.

Currently, the introduction of deep reactive ion etching (DRIE) process provides a powerful tool for bulk micromachining to etch very deep trenches (up to depth of 500 μm) with nearly vertical sidewalls [131, 132]. DRIE is evolved from the need of anisotropic etching trenches with high aspect ratios at a high etch rate. The high selectivity to silicon dioxide for the DRIE process makes it possible to etch deep trenches and stop on a buried layer of silicon dioxide e.g. silicon-on-insulator (SOI) wafers.

For wet bulk micromachining, the features are sculpted from the bulk material such as silicon, SiC, quartz and glass; by orientation-dependent (anisotropic) or orientation-independent (isotropic) wet etchants. Isotropic etchants will etch in all crystallographic directions at the same rate, and are usually acidic in nature e.g. HNA ($\text{HF}/\text{HNO}_3/\text{CH}_3\text{COOH}$). Isotropic etching will produce rounded isotropic features in single-crystal silicon. The simple KOH water system is the most popular etchant used for the case of anisotropic etching of single-crystal silicon. In near saturated solutions (1:1 in water by weight) at a temperature of 80 °C, this etching method produces a uniform and bright surface. The solution attracts $\{1, 1, 1\}$ plane types, which have a high bond density, in a much slower rate than other plane types (the side wall of $\{1, 1, 1\}$ is at an angle of 54.74 ° to the surface) [127]

Bulk micromachining is a relatively straightforward process that does not require elaborate equipment. Nevertheless, this method has its disadvantages. The etchant chemicals commonly used in bulk micromachining are often incompatible with IC or IC fabrication equipment. In addition, bulk micromachining inherently consumes an inordinate amount of wafer surface area as compared to other technologies, and is usually more costly. However, despite these limitations, silicon bulk micromachining is still the most widely used micromachining technology, and this trend will probably continue to be so for the immediate future.

2.3.2 Surface Micromachining

Surface micromachining is a microfabrication process whereby the micromechanical structures or devices are made or built entirely on the surface of the wafer without penetrating the wafer surface. Surface micromachining is an additive process. Typically, the desired micromechanical structure is built up by depositing and patterning thin-films of both structural and sacrificial material on the substrate surface. The most commonly used structural layer is polysilicon (Poli-Si) or silicon nitride (Si_3N_4) [127].

Figure 29 illustrates a generic surface micromachining process flow of a doubly-anchored polysilicon bridge. First, a sacrificial material such as silicon dioxide (SiO_2) or PSG (Phosphosilicate glass) is deposited onto the substrate. The purpose of this sacrificial material layer is to provide a

temporary stand-off from the substrate during the subsequent processing to form the structural layer. After deposition, the sacrificial layer is etched into the desired pattern. Openings are etched entirely through the sacrificial layer so as to provide anchoring points for the structural layer. This prevents the structural layers from ‘floating’ away during the release step at the end of the process. Next, a thin-film layer of the structural material is deposited and etched. After etching, the sacrificial layer is removed by immersion into a wet etchant, thereby leaving behind the released structural layer [133].

Figure 29: Surface Micromachining Process

The key advantage of surface micromachining is its compatibility with conventional IC processing. Surface-micromachined and micromechanical devices are fabricated using standard IC thin-film deposition and patterning technologies without resorting to potentially contaminating chemicals or non-standard processes. Another advantage of surface micromachining is that the size of the devices is not constrained to the minimum device

dimensions. Instead, surface micromachined devices can be reduced to a much smaller size than that made with bulk micromachined components.

The major advantage of surface micromachining is that the technology is inherently a two-dimensional planar process that can possibly limit the flexibility of the design. Surface micromachining is a relatively new technology compared to bulk micromachining, and has not been widely employed in commercial production. However, it is expected to become a preferred method of fabrication in the future due to cost savings and compatibility with integrated circuit processing.

2.4 Main Fabrication and Characterization Techniques

2.4.1 Fabrication Techniques

Preparation of Substrates Before Patterning and Deposition

Most cleaning methods can be loosely divided into two big groups: wet and dry methods. Liquid chemical cleaning processes are generally referred to as wet cleaning. A combination of solvents, acids and water is used to spray, scrub, etch and dissolve contaminants from wafer surface. On the other hand, dry cleaning processes use gas phase chemistry, and rely on chemical reactions required for wafer cleaning. Generally, dry cleaning technologies use less chemicals and are less hazardous for the environment but they do not perform as well as wet methods especially for particle removal. The

method used in this project is mainly wet cleaning. The steps taken are mentioned below:

(1) The wafers are soaked in a SPM bath, which contains sulfuric acid, hydrogen peroxide, and deionized water ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$). The bath is maintained at approximately 110 to 130 °C. SPM is usually used to remove organic contaminations and is often called "piranha clean".

(2) The wafers are then rinsed in deionized water in an overflow rinser. An overflow rinser is a tank with a top spray inlet, a dump valve similar to a dump rinser and a tank within a tank design to allow the rinser to overflow. The tank is initially full when the wafer is being put in. When the process starts, the bottom dump valve opens and empties the water in the tank. Once the tank is empty, clean deionized water is being sprayed onto the wafer cleaning it and filling the tank at the same time as shown in Figure 30 below. The action of the overflow rinser is gentler and provides a less aggressive chemical removal process and also a lower tendency to deposit particles.

Figure 30: Schematic Diagram of Overflow Rinser

(3) The wafers are then sent into the spin rinse dryer for drying. The schematic of the spin rinser dryer is shown in Figure 31 below. Deionized water is being sprayed onto the spinning wafers at low speed. After a preset time, the water rinsing stops and nitrogen is being introduced and the wafers spin at high speed to remove all the water on the wafers.

Figure 31: Schematic Diagram of Spin Rinse Dryer

Photolithography

Photolithography or optical lithography is a process used to transfer a pattern from a photo mask to the surface of a substrate.

A cycle of a typical silicon lithography procedure would begin by putting the substrate in a primer; this step is used to ensure the adhesiveness of the photoresist on the substrate. A layer of photoresist is spin coated onto the substrate by a spin coater. A transparent plate with opaque areas printed on it, called a photo mask or shadow mask, is placed between a source of illumination and the wafer, selectively exposing parts of the substrate to

light. Then the photoresist is developed, in which areas of exposed photoresist will be washed off.

Most types of photoresist are available in "positive" and "negative" forms. With positive resists the area that is opaque (masked) on the photo mask corresponds to the area where photoresist will remain upon developing. Negative resists result in the inverse, so any area that is exposed will remain, while any areas that are not exposed will be developed. After developing, the resist is usually hard-baked before subjecting to development.

Lithography is used because it affords exact control over the shape and size of the objects it creates, and because it can create patterns over an entire surface simultaneously. Its main disadvantages are that it requires a substrate to start with, it is not very effective at creating shapes that are not flat, and it can require extremely clean operating conditions.

CNT Catalyst Deposition Using Electron Beam Physical Vapor Deposition

Figure 32: Schematic of E-Beam Evaporator

Electron Beam Physical Vapor Deposition or EBPVD is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The schematic is shown in figure 32 above. The electron beam causes atoms from the target to transform into the gaseous phase. These atoms then condense into solid form, coating everything in the vacuum chamber.

In an EBPVD system, the deposition chamber is evacuated to a pressure of 10^{-6} Torr. The material to be evaporated is in the form of pellets. Electron beams can be generated by thermionic emission, field emission or the anodic arc method. The generated electron beam is accelerated to a high kinetic energy and focused towards the pellets. When the accelerating voltage is 5 kV and the beam current is a few milli-amperes, 85% of the kinetic energy of the electrons is converted into thermal energy as the beam bombards the surface of the pellets. The surface temperature of the pellets increases resulting in the formation of a liquid melt and evaporates and condenses on the substrate.

PECVD CNT Growth

Figure 33: PECVD System

Figure 33 above shows the Plasma Enhanced Chemical Vapor Deposition system used in the experiment. This system was manufactured by Nanoinstruments Pte. Ltd., a Cambridge based company that deals with manufacturing of CVD systems. The system consisted of a 4-inch diameter isolated substrate heater with a maximum temperature of 800 °C. The process gases supported by the system were NH_3 and C_2H_2 , with mass flow controllers controlling the flow of gases up to maximum concentration of 500 sccm for each of the 2 process gases. Pressure sensor consists of a micro-piranhi, allowing the reading of base pressure and piezo, which allows gas independent pressure reading during process. The heater control consisted of a fully programmable ramp segment. The plasma generator used was a 1 kw dc power supply.

PECVD has been investigated extensively recently by researchers due to its ability to produce aligned CNT. The PECVD first emerged in use because certain processes cannot tolerate the high wafer temperature of the thermal CVD. The low temperature operation is possible because the precursor dissociation is enabled by the high energy electrons in the plasma. For CNT, the precursor dissociation occurs at the surface of catalyst particles producing carbon needed for CNT growth. The true role of plasma in CNT growth is still not clear although there is evidence that the electric field in the plasma enables more vertically aligned CNT compared to thermal CVD.

The eventual particle size and resultant CNT diameter seem to correlate to catalyst film thickness. Thinner films will more likely than not lead to smaller particles and tube diameters.

The process of plasma enhanced chemical vapor deposition is similar to that of thermal CVD. A cleaned substrate (usually silicon or glass) is coated with a metal that has been shown to act as a catalyst for CNT growth, such as Ni, Fe, Co, etc., using various deposition methods (e-beam evaporation, sputtering, etc.). The coated samples are placed into the PECVD reactor, which is then pumped down to a low base pressure (~2 mbar). The carbon containing and reacting gasses are introduced into the chamber through a network of mass flow controllers to regulate the flow rate and gas composition of the mixture. The high voltage causes an ionization avalanche resulting in plasma formation, which acts to decompose the gas into its components. Finally, the carbon is precipitated out of the catalyst in the form of a CNT. This method has more variables than the other techniques

and allows for independent control of growth parameters. It has been shown that substrate temperature, catalyst thickness, chamber pressure, precursor flow rate, gas ratio, order of gas introduction, applied high voltage and current, and electric field orientation have effects on CNT growth rate, diameter, and alignment.

Sputtering of Top Layer Film on CNTs

Figure 34: Schematic Diagram of Sputtering

Sputtering is largely driven by momentum exchange between the ions and atoms in the material, due to collisions as shown in figure 34 above. Although the first collision pushes atoms deeper into the cluster, subsequent collisions between the atoms can result in some of the atoms near the surface being ejected away from the cluster. The number of atoms ejected from the surface per incident ion is called the sputter yield and is an important measure of the efficiency of the sputtering process.

The ions for the sputtering process are supplied by plasma that is induced in the sputtering equipment. In practice a variety of techniques are used to modify the plasma properties, especially ion density, to achieve the optimum

sputtering conditions, including usage of RF (radio frequency) alternating current, utilization of magnetic fields, and application of a bias voltage to the target.

Reactive Ion Etching (RIE) of Top Layer Film

Figure 35: Schematic Diagram of Reactive Ion Etching

Reactive ion etching (RIE) is a technology using plasma to etch material deposited on wafers. The RIE system consists of a cylindrical vacuum chamber with a wafer holder position at the bottom portion of the chamber as shown in figure 35. Gas flow is introduced through small inlets at the side of the chamber and is evacuated out to the vacuum pump system through the bottom of the chamber. The types and amount of gas used are determined by the etch process; for example, oxygen is used for descumming of photoresist after developing and CF_4 is used for etching silicon.

Plasma is initiated in the system through the use of radio frequency (RF) power applied to the wafer holder. The RF power creates an oscillating electric field that ionizes the gas molecules by stripping them of electrons, creating plasma. The dissociated gas ions react chemically with the materials on the surface of the samples, but can also physically etch some material due to their high kinetic energy. Due to the mostly vertical delivery of reactive ions, reactive ion etching can produce very anisotropic etch profiles.

Etch conditions in an RIE system are very much dependent on the many process parameters, such as pressure, gas flows, and RF power.

2.4.2 Characterization of CNTs Film Growth.

Scanning Electron Microscope (SEM) for Surface Morphology Analysis

Figure 36: Photo of Scanning Electron Microscope

Figure 37: Schematic Diagram of SEM [134]

The photo of the SEM being used is shown in figure 36 above and a schematic is shown in figure 37 above. In the SEM, electrons are thermionically emitted from a tungsten cathode and are accelerated towards an anode. Tungsten is used because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by up to two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam in a raster fashion over a rectangular area of the sample surface [134]. Through these scattering events, the primary electron beam effectively spreads and fills a teardrop-shaped volume known as the interaction volume [135], extending from less than 100 nm to around 5 μm into the surface. Interactions in this region, lead to subsequent emission of electrons, which

are then detected to produce an image [134, 136]. Interactions in this region lead to the subsequent emission of electrons, which are then detected to produce an image.

The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. A scintillator-photomultiplier device detects the electrons and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a Digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which result in images with a well-defined, three-dimensional appearance. The SEM system used in the experiment is JEOL-5910L.

Raman Spectrometer for I_D and I_G Peak Detection in CNTs

The Raman Spectrometer schematic is shown below.

Figure 38: Raman Spectrometer [134]

Raman spectroscopy works under the principle of inelastic scattering of light [134, 135]. When a beam of light is incident on an atom or molecule, the atom absorbs that energy before transporting itself to a higher energy condition [137]. The atom that has absorbed the energy immediately tries to release the exact same amount to return back to its ground state. This phenomenon is called Rayleigh Scattering. Alternatively Raman scattering may occur which leads to the atom emitting greater or lesser energy and thus causing the atom to sit at an energy level lower or higher than the ground state respectively. This differential energy then gives rise to two distinct lines on the frequency spectrum called the Stokes and anti-Stokes lines. The frequencies of these lines being a function of the energy difference are thus related to the vibration frequencies of the atoms or molecules. In Figure 38

above, a graphical representation of the Raman Spectrometer is shown. In a Raman spectrometer, the laser beam is focused using an assortment of lenses and slits. The laser beam that is reflected of the sample is passed through a notch filter, which blocks a predetermined range of wavelengths. The laser beam is then diffracted off a grating crystal where the wave numbers are resolved for the spectra. The spatially resolved wave numbers strike a CCD detector where the intensity of each wave number will be a function of the possible vibrational frequencies [135]. Breathing modes relate to vibrations along the radial axis of the nanotube while tangential nodes relate to vibrations along the graphene plane [135]. In the following section, details relating to the experiments conducted will be presented.

Chapter 3: Density Control of CNTs Growth

3.1 Introduction

In this chapter, detailed experimental procedures for the growth of the CNTs. SEM images are used to characterize the samples. In order to work towards the goal of achieving density controlled CNT growth, the first step taken is to identify the CNT that can be grown by varying different conditions such as different catalyst thickness, different etching time, different growth pressure and different deposition time. Nickel catalyst is deposited using e-beam evaporator and has been used for all the experiments conducted. All CNTs in the report are grown using Nano Instruments Plasma Enhanced Chemical Vapor Deposition (PECVD) system. Micrographs of the scanning electron microscope images are taken using JEOL JSM-5910LV. Raman analysis are taken using the Reinshaw micro raman with an argon laser of wavelength 514.5nm.

3.2 Study of Growth Parameters on Quality of PECVD CNTs

An overview of the CNTs growth is shown in the table 2 below. The standard parameters that are being kept constant are deposition temperature 600°C, deposition pressure 12mbar, acetylene flow : ammonia flow 60:240, deposition time of 10 minutes, 10nm thick nickel catalyst, 0 minutes of NH_3 plasma treatment and 0 minutes pre-annealing.

Deposition Temperature (°C)	Deposition Pressure (mBar)	Acetylene Flow : Ammonia Flow	Deposition Time (minutes)
500	9	15 : 240	15
600	11	30 : 240	30
700	13	45 : 240	45
800	15	60 : 240	60

Table 2: Variation of Process Parameters.

3.2.1 Influence of Deposition Temperature

The CNTs were grown at four different temperatures while all other growth process parameters are kept at the standard values. High temperature is one form of drive that provides the energy needed to dissociate the feed gases and the formation of bonds. The SEM images are shown below.

Figure 39: CNTs Grown at Different Temperatures

It was observed that there were no CNTs grown at 500 °C. Figures 39(b) to (d) show the general morphology of the CNTs grown at 600 °C, 700 °C and 800 °C.

At 600 °C, the CNTs had a stunted growth with some variation in the diameters of the tubes. The general morphology of the CNTs grown at the lower temperature of 600 °C also shows very little amount of clustering order within the CNTs. The average height of the CNTs is approximately 0.6 μm and the average diameter of the CNTs is approximately 0.4 μm . On closer inspection, the CNTs are not very well aligned and sparse in density. Moreover there are patches of areas where there are no CNT growth. There are also areas with CNTs that are generally thin and long as compared with the majority of CNTs grown. It was also noticed that some thin and long CNTs tends to buckle under their own weight. The most likely explanation for this may be because of the Van Der Waals forces that cause the thin fragile CNTs to collapse upon contact with neighboring CNTs. Another plausible reason for the collapse may be due to the thin CNTs collapsing under their own weight.

Another observation made is that some CNTs are slightly bent although little in numbers and can be considered negligible as compared with the rest of the CNTs grown. The alignment of the CNTs is vertical in general but the ordering of the CNTs is random in nature especially with respect to the clustering of the CNTs that is very minimal. From the SEM image, the sparseness of the CNTs is clearly evident, with the bald patches shown.

Comparison between the CNTs grown at a temperature of 600 °C and 700 °C shows that those grown at the latter temperature have a higher growth rate. Unlike the CNTs grown at 600 °C, those grown at 700 °C are more dense and clustered. The length of the CNTs is measured using the ruler function in the SEM software and several CNTs are measured and the average length of the CNTs is taken to be approximately 1 μm .

The SEM images taken in figure 39(d) are taken at magnifications of 20,000 times at a temperature of 800 °C and show the general distribution of the CNTs on the sample. It is interesting to note the relative uniformity in the diameter of the CNTs grown as compared to those grown at the lower temperatures of 600 °C and 700 °C. The CNTs are also well aligned and clustered together. The CNTs length is comparatively longer than those grown at lower temperatures and the amount of collapsed CNTs are also lesser in quantity. The average length of the CNTs is approximately 2 μm .

Raman Analysis Results

The Raman spectrums for the CNTs grown at the various deposition temperatures from 600 °C to 800 °C are shown in the figure 40 below.

Figure 40: Raman Spectra of CNTs Growth at Various Deposition Temperatures

The peaks were situated within the range of 1550 cm^{-1} and 1600 cm^{-1} corresponding to G band range and there was a peak situated within the range of 1350 cm^{-1} and 1400 cm^{-1} which correspond to the D band range. These peak values together with the SEM images shown earlier confirmed the presence of CNTs at the various temperatures except $500\text{ }^{\circ}\text{C}$. There were no radial breathing modes that are associated with single-walled CNTs hence indicating that the CNTs were multi-walled in nature.

Table 2 below shows the G band and D band Raman shift values for the different temperatures.

	600°C	700°C	800°C
G-Band peak (cm^{-1})	1591.8	1588.2	1589.6
D-Band peak (cm^{-1})	1397.0	1394.2	1375.0

Table 3: G and D Band Peaks at Various Deposition Temperatures.

Figure 40 shows a typical spectrum of the CNTs raman analysis graph. A Gaussian fit is done using the provided software in the raman system to separate the D and G peaks into two separate graphs. The D and G peaks are characteristic of the sp^2 sites of all disordered carbons at 1350 and 1570 cm^{-1} , respectively. Development of the D band indicates disordering of graphite but ordering of an amorphous carbon structure; its intensity is proportional to the number and size of sp^2 clusters (for CNTs, that is the defects, caps and a-C:C), while its width is more related to a narrower distribution of clusters with different order and dimensions. The G band of graphite involves the in-plane bond-stretching motion of pairs of carbon sp^2 atom; (CNTs body). The I_D/I_G ratios were then calculated by taking the ratio of the areas under the two separated graph and presented below.

Figure 41: I_D/I_G ratio for effects of temperature

From figure 41 above, it was observed that there is a drop in the I_D/I_G ratio from 600 °C to 700 °C indicates a decrease in the defects within the CNTs at the higher temperature. The lower I_D/I_G ratio also indicates that the CNTs are highly graphitized. From 700 °C to 800 °C, the I_D/I_G ratio shows an increase. It is thought that structural defects such as the presence of the particle at the tip is prominent hence increase the I_D/I_G ratios. Thomas W. Ebbesen [185] also suggested that such defects were present in arc-produced CNTs at very high plasma temperature. The reason being that due to the rapid growth of CNTs at high temperature, these results in a temperature gradient in the deposit and there was insufficient time allowed for annealing. Hence the kinetics of formation dominates over the thermodynamics in the growth process of the CNTs [185]. This might be another plausible reason for the high defect content present in the CNTs grown at a high temperature.

3.2.2 Influence of Deposition Pressure

The SEM images of the surface morphologies of the CNTs grown under the various deposition pressures are shown in Figure 42 below.

(c) 13mbar

(d) 15mbar

Figure 42: CNTs Grown at Different Pressures

At 9 mbar, it can be seen from the SEM images that the CNTs are relatively dense. The length of the CNTs is approximately 600 nm. The CNTs grown under the pressure of 9 mbar are non-uniform in diameter and not well aligned. There is no presence of any collapsed CNTs even though there is evidence of a low amount of clustering among the CNTs.

Figure 42b show the growth of CNTs at a deposition pressure of 11 mbar. The growth rate of the CNTs is higher than that of 9 mbar. The CNTs are longer and thinner than those grown at 9 mbar. The CNTs are however less well aligned as compared to the CNTs grown at 9 mbar. The CNTs appears entangled and distorted with high growth density. The entangled CNTs can be explained by the fact that the thin CNTs experience larger Van der Waal's forces resulting in mutual attraction between the CNTs. The higher aspect ratio of the CNTs has also resulted in substantial bending. The diameters of the CNTs are generally uniform and there is also evidence of collapsed CNTs, which is probably due to the thin and fragile nature of the CNTs grown.

SEM images from Figures 42(c) show the CNTs grown at pressure of 13 mbar. The CNTs morphology at the pressure of 13 mbar is very similar to that grown at 11 mbar. The CNTs grown at pressure of 13 mbar are long and thin. The alignment of the CNTs is distorted with evidence of collapsed CNTs due to the high growth rate. The CNTs length is higher than those grown at 11 mbar with the height of the CNTs approximately 2 μm .

SEM images in Figures 42(d) show the morphology of the CNTs fabricated at a growth pressure of 15 mbar. The morphology of the CNTs is similar to those grown at 11 and 13 mbar. However, the growth rate at 15 mbar is higher than those at the lower pressure and this is evident from the SEM images that show a large amount of collapsed CNTs. This is due to the higher growth rate that results in longer CNTs hence the tubes buckle under their own weight. It is also noted that the growth rate is inversely proportional to the diameter of the CNTs. The thinner CNTs indicate a higher growth rate than those of thicker ones. It is also noted that at higher growth rate, the alignment of the CNTs become distorted and there is evidence of clustering of the CNTs. The general trend is an increase in growth rate of CNTs with an increase in growth pressure.

Raman Analysis Results

Figures 43 below show the Raman spectrum for the various deposition pressures. Just as for the other process parameters studied, the absence of the radial breathing modes was noted. The absence of the radial breathing mode indicates that the CNTs grown were multi-walled in nature.

(a) 9mbar

(b) 11mbar

(c) 13mbar

(d) 15mbar

Figure 43: Raman Spectra of CNTs Growth at Various Deposition Pressures

	9 mbar	11 mbar	13 mbar	15 mbar
G band peak (cm ⁻¹)	1588.7	1591.0	1591.8	1593.8
D band peak (cm ⁻¹)	1392.1	1381.0	1397.0	1386.2

Table 4: G and D Band Peaks of CNTs at Various Deposition Pressures

Figure 44: I_D/I_G Ratios of CNTs at Various Deposition Pressures

It is evident from the SEM images shown earlier that an increase in deposition pressure results in an increase in CNTs length. This increase in growth rate has also been reported by Chhowalla [161]. From Figure 44 above, the increase in deposition pressure results in a drop in I_D/I_G ratio. This drop in I_D/I_G ratio is evident from 9 mbar to 13 mbar, which indicates good quality CNTs with minimum defects. The sudden increase in the I_D/I_G ratio at the deposition pressure of 15 mbar can be attributed to the high defect content in the CNTs. At the high deposition pressure of 15 mbar, more nucleation sites were formed which resulted in CNTs growing extremely close together and competing for the dissociated carbon feedstock. This increased competition for carbon atoms then contributed to a less than perfect graphitization of CNTs resulting in the sudden increase in I_D/I_G ratio at 15 mbar. It is also noted that the cut off for good graphitization of CNTs occurs at 13 mbar. The high I_D/I_G ratio at 9 mbar can be attributed

to the high amorphous carbon deposition which results in a slower growth rate which also evident from the SEM images taken at 9 mbar.

3.2.3 Influence of Acetylene Flow Rate Concentration

The SEMs images of the surface morphologies of the CNTs grown under the various acetylene flow rate are shown in Figure 45 below.

Figure 45: CNTs Grown at Different Acetylene Concentration

SEM images shown in Figure 45(a) above shows the morphologies of the CNTs grown at acetylene (C_2H_2) gas flow rate concentration of 15 sccm while the ammonia (NH_3) gas concentration is kept at a constant flow rate of

240 sccm. The growth temperature was kept constant at 600 °C. It is observed that the CNTs growth is dense. The CNTs are aligned vertically but there is non-uniformity in the diameter of the CNTs. Some tall and thin CNTs are interspersed in between CNTs that have larger diameters. This happens when the nickel catalyst formed islands of particles during the initial etching and annealing process, but there will be some tiny nickel particles that did not form into the huge island of nickel clusters. It is also evident that some of the CNTs are clustered together forming bundles but these are not very apparent throughout the sample. It is also noted that catalyst particles are observed at the tip of the CNTs further confirming the tip growth mechanism that is typical of PECVD system. The average length of the CNTs is approximately 0.8 μm .

SEM image in the above Figure 45(b) shows the “forest” like growth of the CNTs at C_2H_2 flow rate concentration of 30 sccm with the NH_3 concentration remaining constant at 240 sccm. The CNTs grown at this flow rate concentration are greater in length but smaller in diameter as compared to the growth of the CNTs at the lower flow rate concentration of 15 sccm. The thin and long CNT growth is probably one of the reasons for the collapse of CNTs due to the structural weakness of long and thin pillars. Most of the CNTs are entangled together closely, indicating possible strong Van der Waal’s forces between the CNTs leading to the attraction force between each other. This might be another plausible reason for the collapse of the CNTs, with the thin CNTs collapsing and clustering upon coming into

contact with their neighboring CNTs. The average length of the CNT is approximately 1.7 μm .

SEM images from Figure 45(c) shows the growth of CNTs with flow rate of C_2H_2 being 45 sccm. From the SEM images, it can be observed that there is still long and thin CNTs but at a much lesser amount as compared to the ones grown at 30 sccm. There appears to be stub like structures for partial of the CNTs. It can be clearly observed that as the diameter of the CNTs increases, the growth rate decreases as compared to those CNTs that are long and thin. This can be explained by the fact that more carbon molecules are required to form the thicker CNTs than those that are of thinner diameter hence account for the lower growth rate.

SEM images from Figure 45(d) shows the growth of CNTs with C_2H_2 flow rate concentration of 60 sccm with the NH_3 concentration remaining constant at 240 sccm. The SEM images clearly show the difference in morphology between the CNTs grown at the lower flow rate concentration of 15 sccm and 30 sccm and that grown at 60 sccm. The CNTs grown at 60 sccm are stub like in structural dimensions. The CNTs growth is not as dense as that grown at 30 sccm. The diameters of the CNTs are also larger than those grown at 30 sccm. The growth appears stunted with the average length of the tube being approximately 0.6 μm . It is interesting to note that the CNTs length is even lower than that at 15 sccm, indicating clearly that an increase in carbon feedstock gas does not necessarily result in an increase in CNTs growth rate but instead increase the diameter of the CNTs.

Raman Analysis Results

The Raman analysis results for effects of acetylene flow rate concentration on CNTs shown in Figure 46.

Figure 46: Raman Spectra of CNTs at Different Acetylene Concentrations

It is noted that the peaks of the D band varied from 1389.8 cm^{-1} to 1397.0 cm^{-1} while the G band peaks varied from 1590.3 cm^{-1} to 1592.9 cm^{-1} . There were no presences of radial breathing modes that are commonly associated with SWNTs and thus it can be concluded that the CNTs grown were of multi-walled in nature.

The table below shows the G band and D band peaks for different flow rate concentrations of acetylene.

	15 sccm	30 sccm	60sccm
G band peak (cm^{-1}) ¹⁾	1587.7	1587.3	1590.0
D band peak (cm^{-1}) ¹⁾	1393.5	1384.2	1392.8

Table 5: The G band and D Band Peaks for Acetylene Flow Rate Concentration

The I_D/I_G ratios were then calculated and tabulated below. The I_D/I_G ratios of the various acetylene flow rate concentrations are presented below.

Figure 47: I_D/I_G ratio variation with acetylene flow rate concentration

From figure 47 above, it was observed that there is an increase in the I_D/I_G ratios for the higher C_2H_2 flow rate concentrations and this result is similar to that of Chhowalla[161]. The increase can be explained through the fact that as the acetylene flow rate concentration increases, the amount of amorphous carbon that is deposited on the sample also increased and this

results in a drop in the etching rate of the carbon. The stunted growth rate at acetylene flow rate concentration of 60 sccm, which can be clearly seen in the SEM images further reinstates the fact that most of the deposition on the sample takes place as amorphous carbon which in turn lead to a reduction in the growth rate of CNTs. However at a flow rate concentration of 15 sccm, the higher I_D/I_G ratio is attributed to defects within the CNTs due to insufficient carbon concentration for growth kinematics and not to deposition of amorphous carbon as the growth rate is higher than that at 60 sccm. The low I_D/I_G ratio at an acetylene flow rate concentration of 30 sccm coincides with the high growth rate at that particular flow rate concentration.

3.2.4 Influence of Deposition Time

The SEM images of the CNTs grown at different deposition times ranging from 15 to 60 minutes are shown in Figure 48.

(a) 15 mins

(b) 30 mins

Figure 48: SEM Images for CNTs grown at Different Deposition Time

The growth of CNTs at a deposition time of 15 minutes has been extensively discussed in the previous section under the influence of pressure at a nominal value of 13 mbar. The growth of the CNTs is dense with small amount of clustering. The clustering of CNTs becomes more pronounced at the deposition time of 30 minutes, which are shown in Figure 48(b). It is interesting to note the difference in the morphology of the CNTs for the deposition time of 15 minutes and that of 30 minutes. The clustering of the CNTs at a deposition time of 30 minutes is very much evident from the SEM images. The clustering of the CNTs is in the shape of a “pine tree” and this morphology occurs in pocket segments of the sample. The morphology of the CNTs comes about due to the closely grown CNTs thereby forming clusters, and at the same time, the CNTs are also tilted at an angle. This tilt can be attributed to the close proximity of the CNTs grown. The CNTs grown are thin and long with their growth rate expectedly higher than that grown at 15 minutes due to the higher energy being provided for the growth mechanism.

The morphology of the CNTs grown at a deposition time of 45 minutes is clearly seen in Figure 48 (c). The clustering of CNTs is clearly seen at this deposition time of 45 minutes. Upon closer observation, it is also evident that there are some CNTs that have collapsed. The longer CNTs collapse due to gravitational force since they are unable to support their own weight. The tall and thin CNTs also indicate that the higher the growth rate, the smaller the diameter of the tubes. This indicates the higher growth rate at 45 minutes of deposition and a possible inversely proportional relationship between the diameter of CNTs and the growth rate.

Figure 48 (d) shows the morphology of the CNTs grown under deposition time of 60 minutes. The amount of collapsed CNTs is far greater than those grown at deposition times of 30 and 45 minutes. The observations obtained are similar to those of the lesser deposition time with the CNTs being thinner and longer but have more clustering and collapsed CNTs.

The general trend observed as the deposition time was increased was an increase in the height of the CNTs. The increase in growth rate is readily inferred since the catalyst sites are exposed to the carbon source for a longer period of time, which leads to higher rate of diffusion and precipitation of CNTs. It is also observed that the CNTs were clustered together at a deposition time of 30 minutes hence indicating that the CNTs grown are long and thin enough to adhere to each other due to the increase in the Van der Waals forces. This clustering effect is seen clearly at 30 minutes because the CNTs do not collapse upon coming into contact with each other.

It is also noticed the amount of collapsed CNTs is inversely proportional to its diameter. A decrease in CNT diameter also indicates a higher growth rate. This can be explained by the fact that there is an increase in the vertical growth rate as compared to lateral growth rate beneath the catalytic site at a higher deposition time, which thus leads to the thin and tall CNTs that are seen at the deposition time of 60 minutes. There is also an increase in the amount of collapsed CNTs at deposition time of 60 minutes because the CNTs buckle under their own weight when they grow too long. It is also worth noting that the alignment of the CNTs is much distorted as the diameter becomes smaller. Therefore if alignment of the CNTs is crucial for a particular application, the deposition time must be optimized so as to ensure that the growth of CNTs is not too long which will result in an increase in collapsed CNTs.

Raman Analysis Results

Figures 49 below shows the Raman spectrum of CNTs grown for 15 minutes to 60 minutes. Similarly, the absence of radial modes indicates that the CNTs are multi-walled.

(a) 15 mins

(b) 30 mins

(c) 45 mins

(d) 60 mins

Figure 49: Raman Spectra of CNTs with Different Deposition Time

The table below shows the G band and D band peaks for different deposition time for CNT growth.

	15 mins	30 mins	45 mins	60 mins
G band peak (cm ⁻¹)	1588.7	1591.0	1591.8	1593.8
D band peak (cm ⁻¹)	1392.1	1381.0	1397.0	1386.2

Table 6: G and D band peaks for the various deposition time

The I_D/I_G ratios are calculated from the G band and D band peaks for the various deposition times ranging from 15 minutes to 60 minutes and shown in figure 50 below. The ratios are shown below.

Figure 50: I_D/I_G ratios of various deposition times

There were no changes in the I_D/I_G ratios when the deposition time increased from 15 minutes to 30 minutes. The high I_D/I_G ratio is attributed to high defect content and in this case, it is due to the presence of catalyst particle tips that are clearly observable from the SEM images shown earlier. At the low deposition times of 15 minutes and 30 minutes, the cap structure of the CNTs dominate as compared to the graphite structure of the body of the CNTs. The low I_D/I_G ratios at longer deposition times is attributed to a longer time allowed for annealing restructuring of CNTs resulting in well graphitized CNTs.

3.3 Study of Growth Parameters on Density Controlling

In this section, various thickness of nickel catalyst are used throughout the experiments conducted. All different thickness of nickel catalyst are grown together with each varying parameters (ammonia etching and pre-annealing). An overview of the experiments parameters variations conducted are shown below. Deposition temperature is kept at 800°C, deposition pressure 12mbar, deposition time 10 minutes and gas flow of acetylene : ammonia is kept at 60:240.

Nickel Catalyst Thickness (nm)	Ammonia Etching (1 minutes)	Pre-annealing (4 minutes)
5		
10	X	X
20		
50		

Table 7: Experimental Details for Growth Parameters

3.3.1 Influence of Nickel Catalyst Layer Thickness

The SEM images below shows the CNTs grown with different thickness of nickel metal layer ranging from 5 to 50 nm.

(a) 5 nm

(b) 10 nm

Figure 51: SEM Images for CNTs Grown at Different Catalyst Thickness

From the SEM images above, it can be clearly shown that the thickness of the catalyst layer affects the CNT diameter, length, and the density. It can be observed that as the nickel catalyst thickness increases, the diameter of the CNTs also increases. It can be seen that for catalyst thickness 5 nm, the CNTs are very thin and long with diameters as low as 15 nm and lengths up to 500 nm, similar to the results of Ren [138]. From Figure 51(a), the CNTs grown with catalyst thickness of 5 nm show good uniformity in its diameter as compared to those of thicker catalyst. As the catalyst layer thickness increases to 10 nm, the CNTs diameters become less uniform in diameter. As the catalyst layer becomes even thicker, however, the average diameter and the distribution of CNT diameter both increase and they become much shorter in length. The diameter of the CNTs grown using nickel catalyst thickness of 50 nm has a large variations with thick and thin CNTs being clearly shown in the SEM images. It can be observed that the nickel catalyst layer breaks into small islands due to surface tension, as well as the compressive stress due to the mismatch of the thermal expansion coefficients of silicon and nickel [139,140]. These island sizes depend on

the thickness of the initial nickel film, similar to the results of Bower [139]. For the thicker catalyst layer, the breaking of the island seems to be incomplete with some small island of nickel catalyst breaking off from the larger island of nickel catalyst hence resulting in the non-uniformity of the CNTs diameter. It is also the same for nickel catalyst layer thickness of 10 and 20 nm just that it is less noticeable. The wider size distribution of the CNTs for thick catalyst layers is attributed to the non-uniform fragmentation of the catalyst layer during annealing. It is also worth noting that no CNTs are grown in the absence of a catalyst.

Figure 52: Relationship between Nickel Catalyst Thickness and CNTs Diameter

Figure 52 above shows that the average CNTs diameter varies in proportion to the initial nickel layer thickness. The CNTs diameter is much larger than the thickness, indicating that the nickel islands formed before CNT growth have a low aspect ratio. The diameter of the CNTs initially increases steeply with an increase in the thickness of the nickel catalyst layer from 5 nm to 10 nm but slowly tapers off with increasing nickel catalyst layer. This shows

that the nickel island can more easily break up and formed island of catalyst when the metal layer is thin as compared to when they are thin.

3.3.2 Influence of NH₃ Plasma Treatment on Catalyst Layer

Etching can be done on the nickel catalyst in the PECVD system by the usage of plasma with a flow of NH₃ gas. NH₃ plasma is responsible for the fracturing of nickel into clusters and etching of residue nickel particle. This mechanism is thought to be responsible for the fracturing of the nickel cluster and subsequent loss of nickel particles from CNT tips, interrupting the growth of selected CNT without the nickel cluster, CNT growth cannot be continued [138].

In the following experiment, two different conditions are used, one is without etching and the other is with one minute of etching time. This is to determine the effectiveness of the NH₃ etching on the density controlling of the nickel catalyst thereby controlling the density of the CNTs. With the recommended manufacturer's deposition conditions, the experiment is done without etching and with one minute of etching. The other deposition conditions are kept at 12 mbar of deposition pressure, 10 minutes of deposition time as defined earlier in table 7.

SEM images are taken and shown below for the various thicknesses (2, 5, 10, 20 and 50 nm) of nickel catalyst. As the nickel catalyst thickness varies, the etching and fracturing of the nickel island will also varies hence the need for results for various thicknesses.

Figure 53: SEM Images of CNTs Grown With / Without Etching

From the SEM images shown in figure 53 above for the 2 nm samples, it can be observed that there are some traces of CNTs growth before the ammonia etching. However, after 1 minute of etching, it is clear that the substrate is totally empty. This could be that all the nickel metal has been etched away due to the high power plasma since the metal layer is very thin. When all the nickel metal has been etched away, no CNTs growth will take place.

From the SEM images for the 5 nm samples, it can be observed that there is no formation of island of nickel catalyst. Another function of the ammonia plasma is the breaking down of the nickel particles to form big islands of nickel catalyst. In this case, there is no increase of the nickel particles before and after the ammonia treatment. There is also very little etching of the nickel catalyst as the density is still comparatively dense as before etching.

For the 10 nm samples, it can be observed from the SEM images that the density after ammonia etching is very significant. The density of the CNTs has reduced by about one quarter to one third. This could be due to the fact that partial of the nickel particles congregate and formed large islands of nickel catalyst where the smaller particles that are not able to join together are being etched away.

In the SEM images for the 20 nm samples, there is not much change in the density of the CNTs as opposed to the 10 nm samples. There is only a slight decrease in the density of the CNTs most probably due to the fact that the thickness of the catalyst is thicker. Hence the catalyst while forming big islands, and the remaining metal particles are not small enough to be etched away since thicker metal layer formed larger islands.

In the SEM images for the 50 nm samples, it can be clearly seen that the nickel particles have grown in size and the remaining nickel metal is being etched to a slightly smaller profile than their counterparts. Even before etching, the density of the CNTs are also much sparser than those of thinner catalyst layer whereas after etching, the CNTs are relatively far apart from one another.

In general, the individual nickel particle size has also grown much bigger from tens of nanometer to around hundreds of nanometer. With a bigger nickel catalyst, the CNTs grown will be much larger in size but the length will be shorter than those grown by thinner nickel catalyst layer, which has the capability of growing longer [3].

3.3.3 Influence of Pre-annealing of Catalyst

The pre-annealing of the catalyst occurs during when the deposition temperature is being achieved and before the NH_3 plasma is being turned on. This process step will provide energy for the nickel particles to congregate and form bigger islands of nickel catalyst. With bigger nickel catalyst, the diameter of the CNTs grown is predicted to increase in diameter.

In the following experiment, two different conditions are used; one is without pre-annealing, the other with pre-annealing. This step is used to determine the effectiveness of the annealing mechanism and with more congregations of nickel particles, the separation of the CNTs grown will be greater thereby decreasing density.

SEM images are taken and show below for the various thickness (2, 5, 10, 20 and 50nm) of nickel catalyst. As the nickel catalyst thickness varies, the congregation of the nickel particles would varies hence the need for results for various thickness.

Nickel Thickness before annealing	Without Pre-Annealing	With 4 minutes Pre-Annealing
2 nm
5 nm
10 nm
20 nm

Figure 54: SEM Images of CNTs Grown at Different Annealing Time.

It can be observed from figure 54 above that the 2 nm sample that the catalyst layer may be too thin that resulted in the entire metal layer being totally etched away without being able to grow in big island of metal particles. Some of the metal catalyst may have also diffused into the silicon substrate causing no metal catalyst to react with the feed gas to form CNTs.

From the SEM images for the 5 nm thick nickel catalyst thickness, it can be observed that before annealing, the CNTs are very densely packed. Some being so densely packed until the CNTs clustered together due to the Van der Waal's forces. This is not the case for the CNTs that is grown using catalyst layer that has been pre-annealed. In this case, the CNTs grown from the pre-annealed catalyst is less densely packed and this can be proved by the fact that less clustering occurs. Another point to note is that the pre-annealing process seems to have little influence on the diameter of the CNTs.

For the 10 nm thick catalyst layer, the similar effect of less clustering of CNTs can be observed for the samples that have been pre-annealed. This further confirms the fact that the density of the CNTs is much sparse. One more observation that can be seen is that the annealing has caused the nickel metal layer to form big island of particles for CNTs growth with small fragments of metal catalyst breaking off due to its inability to merge with the bigger particles. This effect can be seen by the non-

uniform diameter of the CNTs. The trend of these CNTs is such that there is numerous small diameter CNTs around large sized CNTs. This is due to the small catalyst particles not able to congregate together with the larger sized metal catalyst. There is also a significant drop in the density of the CNTs.

From the SEM images for the 20 nm samples, the samples that undergo annealing clearly reveal that quite a significant amount of catalyst particles manage to congregate together with the smaller particles being etched away by ammonia plasma and diffusion into the silicon substrate. The SEM image after the annealing clearly shows the reduced CNTs density. It is also observed that the uniformity of the diameters of the CNTs is higher than those of thinner catalyst. It is possible that the thicker catalyst enables the metal layer to easily form clusters and particles and has less tendency of having small catalyst particles breaking off. The density of the CNTs is the least sparse among all the other different thickness of nickel catalyst.

From the SEM images for the 50 nm samples, it can be observed that the before and after of the annealing has little difference. The only difference being the CNTs is less dense for the samples that have been annealed. There is also little break away of catalyst particles that previously affected those with thinner catalyst layer.

From the above SEM images, it can be seen that the most ideal result will be the usage of 20 nm thick nickel catalysts with 4 minutes of annealing. This produced CNTs that is the sparsest in density.

3.4 Patterning of Catalyst for CNT Growth

It can be observed from section 3.3 that varying various parameters from thickness of metal catalyst, pre-etching and pre-annealing can control the density of CNTs

growth. In addition, the author wishes to bring it on to the next step by integrating MEMS photolithography technology. With lithography, the metal catalyst can be pattern to smaller size and this allows controlled area of growth with specified pattern that can match designs with the applications.

3.4.1 Patterning of Micrometer Sized Channels Using Positive

Photoresist

Alternative steps are taken to reduce the density of the CNT grown. MEMS technology is being employed with photolithography being used extensively. The micro-sized channels catalyst is being produced by the standard MEMS lift off process. In the first attempt, micro sized channels are used for patterning. Basically, long channels with varying thickness are being patterned using the UV lithography. The pattern width varies from 100 μm down to 2 μm . A schematic of the pattern is being show below in Figure 55.

Figure 55: Micro-Sized Channel Mask for Patterning

The above mask design is being used to pattern the photoresist. The catalyst material is deposited and lift off process is performed leaving the micron-sized channels with metal catalyst. The catalyst is then sent for the CNTs growth process with deposition time of 30 minutes, annealing time of 4 minutes and 1 minute of etch time. The SEM images are taken and shown below in Figure 56.

(a) 2 μm channel thickness

(b) 5 μm channel thickness

Figure 56: 2 μm and 5 μm channel with CNT grown on nickel catalyst

It can be observed from Figure 56 that the 2 μm channels are grown with a lot of CNTs with density not that ideal for top layer creation.

Figure 57: 100 μm channel with CNT grown on nickel catalyst

It can be observed from Figure 57 that the density of the CNT is still not well control. The 2 μm channel still has too many CNT and the density is still not low enough. The 100 μm channel has too many CNT and the density is not sparse enough.

3.4.2 Patterning of Micro-Sized Channels with Platinum Catalyst

From observations from section 3.4.1, it can be seen that the density of CNTs growth using nickel catalyst results in very dense CNTs, although patterning has been done at the limit of the lithography equipment, (smallest feature size allowed is 2 μm) It was clear that the pattern size is not small enough to allow very well controlled density of CNTs. Hence another alternative metal catalyst is being used. Platinum catalyst is attempted by numerous researchers and has shown results that sparse density of CNTs can be grown. Therefore the silicon is patterned with the micro-sized patterns and platinum catalyst is being sputtered on the patterns and lifted off. The samples are then placed in the PECVD for identical growth parameters for CNTs growth. The SEM images are being taken after the CNT growth and shown below in Figure 58.

Figure 58: CNT on Pt Catalyst Micron-Sized Channels

Figure 59: CNT on Pt Catalyst Micron-Sized Channels

It can be observed from Figure 58(a-f) that the density of the CNT is very low as compared to the micron channel with nickel catalyst. From Figure 59 above, it can be observed that the CNT separation is about approximately 3 μm , which is a tremendous improvement over the previous CNT grown which only has an average of approximately 50-100 nm spacing. It can be observed that the CNT quality is not good; the bottom is very thick with a very narrow and thin tip. This will not produce a very good column for a good template for hole in top layer hence despite the excellent density control nature, the usage of Pt catalyst is being abandoned.

3.4.3 Patterning of 2 μm Dots Using Negative Photoresist

With results obtained from section 3.4.2, it is clear that Pt catalyst cannot be used due to the poor CNT quality hence photolithography process similar to section 3.4.2 is used with a mask with 2 μm sized hole patterns. Further process has to be taken for the nickel catalysts. Negative photoresist has been adopted instead of the more commonly used positive photoresist. The

section below illustrates the advantage of negative photoresist over positive photoresist for the lift off process.

Advantages of Negative Photoresist

Next, negative photoresist is used instead of positive photoresist due to its unique properties. By using negative photoresist, the dimension of 2 μ m hole patterns can be manipulated by changing the exposure timing. With increase in the exposure timing, the dot pattern can be reduced in size. Another advantage of negative photoresist is its profile after exposure and developing. This improves and simplifies the lift off success rate. Two schematics below show the difference between positive and negative photoresist.

Figure 60: Difference Between Positive and Negative Photoresist

Figure 60(a-c) above shows the resist profile for the positive photoresist. The hole patterns are transparent on the chrome mask whereby ultra violet light is able to shine through and expose the photoresist. The characteristic of positive photoresist lies in those areas being exposed by ultra violet light will be susceptible to developer and be washed away. Due to the profile of positive photoresist, the side walls of the photoresist will have some metal deposited as shown in Figure 60b. When the photoresist is being washed away by the usage of acetone in the lift off process, the sidewalls which have metals being deposited will collapse causing the metal dots to be bigger than the expected pattern size.

This is not the same for the negative photoresist as shown in Figure 60(d-f). Negative photoresist is exactly the opposite of positive photoresist whereby those areas being exposed will be more resistant to developer. Due to the nature of the negative photoresist profile, it can be clearly understood from Figure 60(e) that there is no problem of having the metal deposited on the sidewalls of the photoresist. Hence in this case, it is more suitable for lift off process than positive photoresist.

Micron-Sized Catalyst Dots

A new mask is being designed with the intention of creating equally spaced micro-sized holes on the silicon wafer. The design of the mask is being shown below in figure 61.

Figure 61: Overall View of Mask Design

Each square cell considers one hundred $2\ \mu\text{m}$ arranged in ten by ten as shown in Figure 62 below.

Figure 62: Close Up of Single Square Unit Cell

The distance between the $2\ \mu\text{m}$ dots are changed. The reason in doing so is to create a variety of spacing to decrease the density and to show the flexibility of the patterning concept. The different spacing is shown in details in Figure 63 below.

Figure 63: Schematic Diagram of Individual Cells

Patterning is being carried out using the mask. Approximately $2\text{ }\mu\text{m}$ thick of negative photoresist is being used. This creates a one to one ratio for the holes, which makes it easy to develop the photoresist, deposition of metal layer and lift off. Several photoresist spin coating and ultra violet exposure timing are being attempted by the author. Ultimately, the ideal recipe for the negative photoresist is attempted A close up shot is being taken using an optical microscope and shown in figure 64 below.

Figure 64: Microscope Shot of Patterned Dots

Below in figure 65 is another close up shot of the dots that has just being patterned before the metal deposition. It can be clearly observed that $2\text{ }\mu\text{m}$ dots are very well defined and are shaped circular without any form of distortion that is typical of small sized features. All the patterns are also being developed without missing pattern dots.

Figure 65: Close Up Shot of Micro-sized Dots

The above sample is being taken for metal deposition using the E-beam evaporator followed by acetone lift off. The samples are then taken for PECVD CNT growth using the condition previously tested. SEM image is taken and shown below in Figure 66 below.

Figure 66: SEM Image of CNT Grown on $2\text{ }\mu\text{m}$ Dots

It can be clearly observed from the SEM image above that there are several problems being faced.

For a start, the previously well defined equally spaced catalyst dots are not being observed here. This could be due to some problems with the acetone lift off process whereby it is possible some of the metal catalyst that was once on the photoresist landed back onto the silicon substrate during the ultrasonic lift off process hence causing some CNTs to grow on the substrate. Another possible reason could be there are some pin holes on the photoresist that did not totally shield the substrate from the metal deposition process.

Another problem faced is that there is more than one single CNT growing on a single nickel catalyst dots. This is possible due to the catalyst dots being approximately 2 μm in size whereas the average diameter of CNT grew under a 20 nm thick catalyst layer is approximately 175 nm. This can be observed from the top left hand corner of the SEM image that there are at least three CNTs in the catalyst dot. However, there is one slightly different result, the CNT diameter is approximately 450 nm as compared to those earlier experiment done on those substrate that is not being patterned. It could be possible that with lesser metal particles instead of layer, it is easier to congregate and formed larger islands of metal catalyst. This is a good finding considering that it is almost impossible to create patterns down to 150 nm in sized with the ultra violet photolithography. The current method needs to be modified and enhanced in order to produce sub-micron sized catalyst patterns. The method is being explained in the next section.

3.4.4 Improvised Method for Patterning of Catalyst Dots

With the combined results from the previous sections, the author realized that several methods can be combined to achieve the intended results. Hence in the hope of achieving low density CNT and with the limitations of the lithography equipment, several processes are used to reduce the size of the catalyst.

By exploiting several unique features of the process and material, an improvised method for the patterning and growth of CNT is being experimented. The steps are being explained below:

- (a) Negative photoresist can be intentionally overexposed to create a smaller pattern size. This is impossible for the positive photoresist because positive photoresist on overexposed, will create a pattern bigger than the intended size (Figure 67a) and being underexposed, will create an incomplete exposure (Figure 67b) leading to the metal layer being removed during lift off process. The two disadvantages of positive photoresist are being shown below.

Figure 67: (a) Overexposed (b) Underexposed Positive Photoresist.

- (b) Nickel metal layer can be annealed to form large islands of particles. As shown in previous sections, annealing decreases the density of the CNT growth due to the congregation of metal particles together.
- (c) Nickel particles can be etched by the usage of ammonia plasma before the growth of the CNT. This step can be used to remove the smaller nickel particles that did not congregate to become larger particles. This step will prevent the CNT growth on smaller left over metal catalyst.
- (d) There will not be any buffer layer being deposited intentionally. This is to purposely allow some portion of nickel metal to diffuse into the silicon layer. Those smaller metal catalysts will diffuse into the silicon substrate and will not cause small CNT to grow.
- (e) The samples are coated with slightly thicker photoresist and ultra sonic lift off twice with immediate IPA rinse to prevent the redeposition of metal particles onto the substrate.

With the abovementioned steps, the correct procedures are listed below schematically.

Firstly, the negative photoresist is being intentionally overexposed as shown in figure 68 below. This will create a hole that is smaller than the actual size after exposure and developing.

Figure 68: Overexposure of negative photoresist

Several trial and error was done before the minimum hole size can be obtained. If the holes are too small, the aspect ratio is too high which will result in failure to fully developed and remove the photoresist in the hole as shown in Figure 69 below.

Figure 69: Undeveloped photoresist

Figure 70: Nickel Catalyst Dots Done by Negative Photoresist

An optical microscope is being used to take an image of the patterns. The slanted photoresist profile can be seen in Figure 70(b) above. The circular pattern that is white in color that is much smaller than the initial black ring, which is the result of the overexposure of the negative photoresist.

After successfully obtaining the recipe for the negative photoresist patterning, nickel metal is being deposited on the patterns and lift off is done. The resulting catalyst dots undergo annealing and etching to remove small catalyst particles and obtain small catalyst dots. The process flow is shown in Figure 71 below. Initially, as shown in Figure 71(a), the deposited nickel layer has undergone lift off and leaves the small particles nickel patterns on the substrate. After annealing, the nickel particles congregate and grow in size as shown in Figure 71(b). At the final step just before the CNT growth, the sample undergoes ammonia etching and heating, tiny metal particles that may be present are either being etch away or being diffused away leaving the resultant as shown in Figure 71(c).

Figure 71: Nickel Catalyst Dots Process.

Figure 72: CNT Grown on Processed Nickel Catalyst Dots

Figure 72 above shows a SEM image taken from the samples that is being processed using the improvised method of photoresist patterning and pre-process steps. It can be clearly observed this time that there is four particular metal catalyst dots that is being evenly spaced out. The other parts of the

substrate are also relatively clean and clear. There are some traces of small CNT but that is not of a problem due to the fact that a 1 μm thick top layer will cover the CNT at a later stage and that will cover up the smaller CNTs.

Figure 73: Single CNT Grown on Processed Nickel Catalyst Dots

Figure 73 above shows the single CNT grown, it can be seen that there is still a very small CNT on the left of the main CNT. Etching time may be increased to remove this small nickel particle but overall, it will not affect the growth of the top layer.

Chapter 4: Deposition / Growth of Thin Film Layer on CNTs

After gathering the conditions for the growth of the CNTs. The next step is the creation of the porous template as shown earlier in figure 2. Three materials are chosen as the top membrane. First is silicon nitride (Si_3N_4) layer which are deposited by two different methods namely Unaxis Nextral D200 PECVD and Tystar low pressure chemical vapor deposition (LPCVD). Next is the silicon oxide (SiO_2) layer that is deposited using Unaxis Nextral D200 PECVD. Lastly is nickel metal which is sputtered using Nanofilm sputterer. All films are characterized using JEOL JSM-5910LV SEM.

4.1 Deposition of Si_3N_4 Layer on CNTs

4.1.1 Deposition of PECVD Si_3N_4

After the CNTs are grown on the silicon substrate, the samples are taken for silicon nitride growth using the process PECVD. This process typically uses low temperature that is a good start for the CNT samples due to the fact that carbon oxidizes at high temperature. The thickness of the silicon nitride layer is chosen to be 1 μm because it will cover part of the CNT which has an average length of 2 μm . This will enable the tip of the CNT to be removed using chemical mechanical polishing (CMP) at a later stage.

Experimental Conditions

For PECVD Si_3N_4 , the process parameters are as follows:

Temperature: 280 °C	NH_3 : 200 sccm
RF Power: 250W	He: 100 sccm
Pressure: 620 mTorr	N_2 : 400 sccm
SiH_4 : 20 sccm	Deposition rate: 550 Å/min

Table 8: PECVD Parameters for Si_3N_4 Growth

It can be observed from the surface of the samples that silicon nitride has been successfully grown due to the color change from matt black surface to reflective bluish green. SEM image need to be taken to further confirm the silicon nitride layer quality.

SEM Results

After the 1 μm thick of Si_3N_4 is grown on the CNT samples, SEM images are obtained from the top view.

(a) 2nm

(b) 5nm

Figure 74: SEM Images of Top View of PECVD Growth Silicon Nitride

It can be observed from the top view SEM images shown in figure 74 that there appears to be a formation of circular balls on the surface of the samples after the silicon nitride growth. Initially, it appears to be contamination of samples during growth but from the 2 nm thick nickel samples where there is no CNT is being grown, it can be observed that a smooth layer of silicon nitride is being grown. This implies that without the presence of CNTs, silicon nitride can grow and form a smooth layer. But with the presence of CNTs beneath, it appears that there is some influence on the growth of the silicon nitride layer. Little can be deduced from the top view of the samples hence the samples are cleaved in the center and side profile SEM images are taken and shown below.

(a) 2 nm

(b) 5 nm

(c) 10 nm

(d) 20 nm

(e) 50 nm

Figure 75: SEM Images of Cleaved View of Si_3N_4 Layer

The SEM images shown in Figure 75 above show the cleaved view of the samples after the growth of Si_3N_4 . It can be clearly seen from Figure 75(a) that there is no CNT layer at the bottom of the silicon nitride layer hence no nano-ball effect can be observed. It can be observed from Figure 75(b-e)

that there are CNTs beneath the silicon nitride layer and the silicon nitride layer on top of the CNTs exhibits the nano-ball symptom. It is also obvious especially in Figure 75(e) that the silicon nitride layer sits on top of the CNTs without filling in the gap. Firstly, confirmation need to be done to make sure that the silicon nitride layer is not being ripped off while cleaving the samples. And lastly, attempts can be made to reveal the tip of the CNT to prepare the samples for CMP.

Etching of the Si_3N_4 is done by Technics Reactive Ion Etching series 800 II (RIE) to try to reveal the tip of the CNT. The purpose of revealing the tip of the CNT is for the purpose of easy removing of the CNT to form top layer with holes. After etching for 5 minutes and the SEM images are shown below.

(a) 2 nm

(b) 5 nm

(c) 10 nm

(d) 20 nm

(e) 50 nm

Figure 76: After RIE etch for 5 minutes

After 5 minutes of RIE etching under plasma power of 300 W and gas flow of 10:1 CF_4 to O_2 , the tip of the CNT is still not being reviewed hence further RIE etching is required. It can be observed that the tip of the CNT seems to be appearing in Figure 76(c-d).

Another 7 minutes of etching is done by the RIE and the SEM images are shown below.

(a) 2 nm

(b) 5 nm

(c) 10 nm

(d) 20 nm

(e) 50 nm

Figure 77: After RIE etch for 12 minutes

From the SEM images shown above in figure 77, it can be observed that the CNTs are still being covered beneath the top layer of silicon nitride layer. A total of 12 minutes of etching is equivalent to approximately 600-800 nm of silicon nitride, this could mean that most of the silicon nitride did not penetrate in between the CNTs and it is possible that the silicon nitride layer just sits on top of the CNT.

Further examinations on the samples are being carried out and one particular spot on the sample reveals evidence of previous deduction.

Figure 78: Non conformity of top layer

From the SEM images taken above in figure 78 in one portion of the sample, it is being revealed that the silicon nitride layer did not penetrate in between the CNTs, the gaps between the CNTs are very 'clean' with no traces of silicon nitride.

Another peculiar behavior of the thin film layer on top of the CNT is shown below.

(a) Direct Top View

(b) Side View of Top Layer

Figure 79: Nano-balls formation

It seems that the silicon nitride layer on top of the CNT shown in figure 79 above has formed into balls instead of a top thin film layer. As mentioned in

the earlier section of this report, the silicon nitride layer formed on surface without CNTs shows very smooth surfaces as opposed to those with CNTs beneath.

Both these phenomena can be explained by the super hydrophobic nature of CNTs [141]. Several researchers have found these observations and one such observation mentioned about the super hydrophobicity of the CNTs is most likely resulted from the secondary roughness due to the large variation in the height of the tall CNTs [141-143]. As shown in Figure 80 below extracted from research papers [142], it can be observed that the water droplet stays on top of the long CNTs proving the super-hydrophobicity.

Figure 80: Suspended Water Droplet on CNTs Forest

The nanoballs formed on top of the CNTs may be due to the super hydrophobicity of the CNTs.

4.1.2 Deposition of LPCVD Si_3N_4

SEM Results

In this section of the report, patterning of nickel catalyst dots samples is being used for the CNTs growth. SEM images are being taken after the silicon nitride deposition by LPCVD. LPCVD is a high temperature process but the CNTs did not oxidize and vaporized due to the absence of oxygen. The higher temperature will also enhance the conformity of the silicon nitride layer due to the high energy state. From the SEM images below in figure 81, it can be observed that the silicon nitride layer has been coated around the CNTs. This can be shown by the increase in the diameter of the CNT from 400-500 nm to approximately 1.2 μm .

Figure 81: SEM Image of Silicon Nitride Deposited Samples

The property exhibited here seems to show hydrophilicity instead of the previous experiment where hydrophobicity is being observed. This could be due to the high surface energy of the graphitic surface of the CNTs that allows the silicon nitride to form on the surface of the CNTs.

Figure 82: Close Up SEM Image of Silicon Nitride Deposited Samples

Further examination of the samples revealed an interesting results and conclusion. On those samples that have multiple CNTs in one-pattern dots as shown in figure 82 above, nano balls can also be observed from the top of the CNT bundles. It seems that the silicon nitride is being attracted to the top of the CNT thereby forming the nano balls.

Figure 83: Surface Tension Schematics

In order to explain this phenomenon, let us look at the Young-Laplace's equation

$$\gamma_{lv} \cos(\theta) = \gamma_{sv} - \gamma_{sl} \quad (6)$$

The surface of any liquid is an interface between the liquid and some other medium as shown in figure 83 above. Surface tension is not a property of the liquid alone, but a property of the liquid's interface with another medium. If a liquid is in a container, then besides the liquid/air interface at its top surface, there is also an interface between the liquid and the walls of the container. The surface tension between the liquid and air is usually greater than its surface tension with the walls of a container. And where the two surfaces meet, they form a contact angle, which is the angle the tangent to the surface makes with the solid surface and their geometry must be such that all forces balance according to the young-laplace's equation.

According to the Wenzel model [144], the surface geometrical properties are governed by the equation 7 shown below where r is the roughness factor.

$$\cos \theta^w = r \cos \theta \dots \dots \dots (7)$$

Figure 84: Wenzel Model Schematic

The resulting schematic is shown above in figure 84, wetting is homogenous and the surface exhibit super hydrophobic due its surface roughness. The rougher the surface is, the higher is the hydrophobicity of the surface.

Another explanation that can be used is the Cassie-Baxter model [145] as shown in figure 85 below.

Figure 85: Cassie-Baxter Model Schematic

According to Cassie-Baxter model, the decrease in fluid-surface contact area increases the hydrophobicity.

With both models mentioned, it can be clearly understood why the silicon nitride layer ‘sits’ on top of the CNTs. Basically, the length of the CNTs are not uniform in length hence causing an increase in the surface roughness and the spacing between the CNTs due to the low density causes the decrease in the contact patch area. Both these effects greatly increases the hydrophobicity of the surface hence the formation of the ‘nanoballs’ effect seen in the SEM images. The air gap between the CNTs also prevented the silicon nitride layer from permeating in between the CNTs as shown in Figure 78. As further prove from Figure 81(b), it can be observed that the silicon nitride layer is able to coat the entire CNT whereas in Figure 82(a) with about four to five CNTs in a bundle, the Wenzel and Cassie model comes into action.

From the side profile of the samples, it can be observed that the thickness of the silicon nitride is approximately 300-400 nm. Hence the author attempts to do mild CMP on the samples. SEM images are taken and shown below.

Figure 86: SEM Image of Surface after CMP

It can be observed in figure 86 above that after the CMP, some of the CNTs have been uprooted from the substrate and in the process, rupture the silicon nitride layer.

Further deposition of the top layer is required to bury the CNT. This is done through several more deposition.

(a)

(b)

Figure 87: Increasing Growth of Top Layer on CNT

It has been demonstrated in Figure 87 that it is possible to submerge the CNT in the top thin film layer and overcome the hydrophobicity effect by growing of single CNT. Although the CNT has been totally coated by a layer thereby increasing its diameter, this should not pose a problem when the top of the CNT is being ‘shaved’ off and the exposed CNT tip can be removed at a later stage.

4.2 Deposition of PECVD SiO₂ Layer on CNTs

4.2.1 Experimental Conditions

For PECVD SiO₂, the process parameters are as follows:

Temp: 280 °C	N ₂ O: 400 sccm
RF Power: 100 W	He: 184 sccm
Pressure: 730 mTorr	Dep rate: ~ 2100 Å/min
SiH ₄ : 30 sccm	

Table 9: Deposition Condition for PECVD SiO₂

4.2.2 SEM Results

SiO_2 is grown by low temperature oxidation (LTO) process because the growth of SiO_2 will require oxygen. This will cause the CNTs to oxidize and disappear when being exposed to oxygen and high temperature environment. Hence low temperature oxidation is being used. 1 μm thick of SiO_2 thin film layer is being grown on top of the CNTs samples similar to section 4.1.1. The SEM images for the grown films are shown below.

(a) 2nm

(b) 5nm

(c) 10nm

(d) 20nm

(e) 50nm

Figure 88: SEM Images of SiO₂ Layer on CNTs

It can be observed from Figure 88 above that the SiO₂ layer also forms nano-balls. The results are similar to that obtained earlier in section 4.1.1. It can also be observed that the silicon oxide did not manage to fill in the gaps between the CNTs, which are reconfirmed to the observation and conclusion of the previous section.

4.3 Deposition of Nickel by Sputtering on CNTs

4.3.1 Experimental Conditions

Nickel is sputter onto the CNTs with length of approximately 1 μm using Nanofilm sputtering equipment. The thickness of the nickel metal is approximately 500nm which is obtained with plasma power of 200 W.

4.3.2 SEM Results

The thickness of nickel was chosen to ensure that the nickel metal layer does not fully cover the CNT that the usage of heat to remove the CNT may be tested.

SEM images are taken and shown below.

(a) 2 nm

(b) 5 nm

(c) 10 nm

(d) 20 nm

(e) 50 nm

Figure 89: SEM Images After Deposition of Nickel Metal

From the SEM images shown on Figure 89, it can be observed that the nickel metal did not manage to fill the gap in between the CNTs. Instead, the nickel metal accumulates on top of the CNTs. It may be possible that some nickel catalyst may have filled in between the gap of the CNTs as shown in figure 90 because the length of the CNTs is much shorter than the initial length of 1 μm .

Figure 90: Close Up SEM of Nickel on CNT Tip

4.3.3 Possible Prospects for Findings

The nickel metal catalyst sitting on top of the CNTs may be used as catalyst for the next level of CNT growth. The schematic of the proposed idea is shown below.

Figure 91: Proposed Idea for Top CNT Growth Concept

The proposed idea is good for producing networking of CNT on the top of the bottom CNT is shown in figure 91 above. This idea is also good for producing flexible mattress structure that cannot be achieved by single CNT structure.

4.4 Deposition of Thin DLC Layers on CNTs

After the CNTs are grown on the silicon substrate, the samples are taken for DLC growth using the FCVA technique. This technique typically uses room temperature that is a good start for the CNTs samples due to the fact that carbon oxidizes at high temperature. The thickness of the DLC layer is chosen to be 5 μm .

4.4.1 Experimental Conditions

The hybrid film was prepared by first growing a dense, vertically aligned, multi-walled CNTs on a silicon substrate. This prepared sample, together with a bare silicon substrate that served as a reference sample, was then placed in an off-plane, double-bend, filtered cathodic vacuum arc (FCVA) system with substrate pulse biasing[146] to deposit a 5 μm DLC film on the surface of the CNTs.

4.4.2 SEM Results

The results of the growth and deposition are shown below.

Figure 92: Dense Bottom CNTs Layer

Figure 93: Thin DLC and CNTs Hybrid Material

It can be observed from Figure 93 above that the DLC successfully ‘sits’ on top of the CNTs and form a uniform film on top of the CNTs shown in figure 92. The reason why ‘nanoballs’ are not being observed here is due to the very thick layer of DLC which cancel out the surface effect.

4.4.3 Discussions

It has been demonstrated that a unique structure that contains aligned CNTs covered with a hard layer of DLC results in a carbon-based damping

material with possible outstanding mechanical properties. By combining highly elastic CNTs with DLC film, a possible new intrinsic damping material can be achieved. Further more, with the damping properties dependant on CNTs density and the diameter of CNTs, adaptations for various applications can be easily made by adjusting these parameters.

4.4.4 Prospects for Findings

Highly sp^3 bonded DLC and CNTs are inherently stable at high temperatures, wear and chemical-resistant. These composites may find application as perfect environmental seals for micro and nano-devices. This seal would not just protect the components from harsh environments but also provide mechanical vibration isolation and wear protection.

4.5 Deposition of Ultra Thick ta-C Layers on CNTs

4.5.1 Experimental Conditions

Approximately 20 μm of DLC is being deposited on the CNTs surface using the same FCVA process as in section 4.4.1. The SEM results are shown below.

4.5.2 SEM Results and Discussions

Figure 94: Thick DLC Layer on CNTs

The SEM results above in figure 94 above shows the 20 µm thick DLC on CNTs. It can be observed from the SEM images that the DLC layer seems to have covered the CNTs. It may be possible that the thicker DLC have compressed the CNTs totally. Further work will need to be done to verify this result.

Chapter 5: Conclusions

From the CNTs density experiments, it has been observed that the increase in the deposition temperature resulted in longer and sparser CNTs but resulted in more defects in the CNTs. CNTs quality improves as deposition pressure increases until the optimum pressure of 13 mbar where after which, the quality of CNTs decreases. The acetylene to ammonia ratio shows an optimum CNTs growth at approximately 1:8. Generally, an increase in deposition time increases the length of the CNTs but decreases the quality of the CNTs. It was shown that there is proportionality between the thickness of the nickel catalyst layer to the diameter and density of the CNTs where the increase in thickness of the nickel catalyst layer increases the diameter of the CNTs but decreases the density of the CNTs. With ammonia etching and pre-annealing before the CNTs growth, it is possible to achieve sparser CNTs growth by choosing the appropriate parameters combinations. Patterned nickel catalyst with CNTs growth has been demonstrated and through the use of a new improvised method of ultra violet lithography, it has been demonstrated that it is possible to grow single CNT. Silicon nitride and silicon oxide has been deposited on the top of the CNTs and ‘nanoballs’ effect was observed and explained using the Wenzel and Cassie model where surface properties affect the hydrophobicity of the CNTs surface. Nickel metal deposited on the CNTs has shown prospective future research area. Thin DLC layer has been successful deposited on CNTs. This proves the concept of the idea of creating a hard surface yet has a damping effect. The thick DLC layer on CNTs has to be further investigated.

Chapter 6: Future Works / Recommendations

Future works include the statistical calculation of density of CNTs by calculating the area of CNTs versus the area of the sample. This will provide clearer process parameters which are useful for future CNTs works.

The conversion of CNTs surface to become hydrophilic can also be explored to allows a conformal top layer to be produced hence producing a more even layer template.

New ways can be developed to remove the CNTs in the thin film layer as present CMP is not able to successfully remove the CNT without damaging the surface of the thin film layer. The new way should have a low removing rate in order not to damage the thin film layer.

Further experiments can be done on the nickel on the tip of CNT. The samples can be experimented to try to grow CNTs on top of the tip of the CNT so as to achieve a better damping material for the DLC-CNTs hybrid material.

Thick DLC layer on CNTs have to be further investigated to understand the physics and resultant for the disappearance of the CNTs after the thick DLC growth. The DLC layer on CNTs has a lot of future prospect due to integration of hard and soft materials together and multilayers of these materials can be further explored.

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