Growth and Deterministic Assembly of Single Stranded Carbon Nanotube

by

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Abstract

The ability to control the shape, position, alignment, length and assembly of carbon nanotubes over large areas has become an essential but very difficult goal in the field of nanotechnology. Current assembly efforts for nanostructures (such as carbon nanotubes) are mostly based on the concept of planting seeds and growing them into nanostructures, which cannot integrate nanostructures to micro/macro structures deterministically in a long-range order. So to overcome the problem of assembly at nanoscale, this thesis investigates a new way of growth and assembly of nanostructures (carbon nanotube). This process is termed as nanopelleting, which refers to control length, alignment, handling and transportation of a nanostructure (carbon nanotube).

Nanopelleting is a new concept to embed nanostructures into assemblable micro-blocks, and then have them individually transplanted, located and assembled. This method includes vertical growth of single strand carbon nanotubes, pellet casting, planarization, pellet separation, transplanting and bonding. A new CNT PECVD machine has been designed and built to custom fit to our specifications for vertically grown single strand CNTs. We have built a dc plasma reactor because it is simple to build and the growth mechanism of CNTs is optimal. By embedding a single strand CNT in a cylindrical SU-8 pellet, a high aspect ratio pellet (nanocandle) is fabricated. The sizes of the pellets are 75-100um diameters, so they can be easily handled and transported to the required location.

As an application of this nanopellet, we report the concept of an in-plane AFM probe specifically designed for the needs of imaging biological samples with its low stiffness and high-aspect-ratio tip. The designed and fabricated pellet is also used as a nanotemplate to transduct thermal nano-dots in a desired pattern on a large surface area.

Thesis Supervisor: Sang-Gook Kim
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This research project involved building of carbon nanotube machine and the use of many different machines. I like to thank Jeung-hyun Jeong, Kurt Broderick, Luis, Hyung Woo Lee, Soohyung Kim and Wonjae Choi for helping me to build robust carbon nanotube machine. Also, thanks to Mark Mondol, Dave Terry, and Paul Tierney for training on various equipment at the Microsystems Technology Laboratories.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Sumino Iijima in 1991 [1] discovered that carbon formed extended tubular structures in the soot of arc-discharge evaporator. Since then, many researchers around the world have shown great interest in carbon nanotubes due to their remarkable electrical, mechanical, chemical and thermal properties [2]. These properties have made CNTs of potential interest for a large variety of engineering applications including field-emission devices, hydrogen storage, nanoelectronics, chemical sensors, biosensors and scanning probes [3-5]. Currently, two types of carbon nanotubes are available: multiwalled carbon nanotube (MWCNT) and single-walled carbon nanotube (SWCNT). MWCNTs usually have outer diameter of 50-200nm and around 10 micrometer long while SWCNTs are thinner, 1.0-4.0 nm in diameter and around 100 micrometer long.

MWCNTs and SWCNTs are grown by many methods such as: arc discharge [6], pyrolysis, laser ablation [7] and chemical vapor deposition [8], all of which involve high growth temperature and often lead to random orientation. Hence it is laborious to separate, handle, purify, orient and cut to required length before use CNTs for any specific applications. Among various CNTs growing methods plasma enhanced chemical vapor deposition (PECVD) has received considerable attention because it can produce vertically aligned multiwalled nanotubes at a relatively low temperature with a high yield. This technique utilizes a bulk growth process suitable for large-scale manufacture producing unpatterned carpet of CNTs followed by purification and fluid dispersion to provide high yield. The main limitation of this technique has been there was no control of CNT placement and specific geometry. Recently, Z. F. Ren's group [9] has demonstrated that is possible to grown patterned individual CNTs with controlled location and density. This result has been developed further is this thesis to produce large-scale growth of nano-scale structures (CNTs) with control in location, shape and orientation for making many nanoscale devices used for applications in scanning microscope, nanoelectronics and

biological probes. The key challenge to make these nanoscale devices is to transport and integrate an individual nanostructure (CNT) at specific location on the device.

To address these challenges, we have developed a manufacturing process termed as nanopelleting [10-12], which refers to transplanting and assemble of CNTs deterministically. This technique includes vertical growth of single carbon nanotubes, pellet casting, pellet separation and transplantation for making functional nano devices. We are now certain that nanopelleting is a new nano-manufacturing technology to assemble and integrate nanostructures to microstructures, creating novel functionalities in macro-scale systems: i.e. nanopelleting is the technology for the multi-scale manufacturing. Nanopellets can easily be positioned by MEMS manipulator or fluidic self-assembly systems. The bulk of nanopellets will then be released after the assembly to expose nanotubes. One immediate application will be the carbon nanotube emission-tip array uniformly spaced over a large substrate, which will enable commercialization of field-emitting displays, multi-e-beam writers and massively parallel SPM tips.

The key idea of our technology in making the proposed system is to assemble nanostructures deterministically at the location where it is needed, such as to assemble a single strand carbon nanotube to the tip of a micropipette (or the tip of an AFM probe), which then can be positioned precisely by an AFM device. A single strand carbon nanotube (MWNT) is to be assembled as a high-aspect-ratio tip of the in-plane MEMS device. The in-plane AFM probe also has a great potential for building a massively parallel scanning probe array. The in-plane structure would also enable possible integration of micro-fluidic, photonic and electronic channels to the scanning probes for the delivery of reagent and transduction of photons and electrons from/to bio structures. One of the potential applications is the use of the nanoscanning system to the Raman spectroscopy of single molecular bioassays. In order to improve Raman spectroscopy, a metal-coated CNT tip can be brought into contact with a sample surface. This will provide much enhanced and highly localized Raman scattering signal and offer a more uniform enhancement when scanning over the molecular scale sample. It is also expected that the CNTs' plasmonic behavior and the variable stiffness of the in-plane probe can further enhance Raman signals, thereby providing a high enough sensitivity for the imaging of single molecular structures, such as proteins.

The focus of this thesis is to develop the nanopelleting concept by building robust CNT machine, develop suitable process steps to grow single stranded CNT, fabricating nanopellets and investigating the transplanting of nanopellets. The results obtained demonstrate that nanopelleting is a feasible method of controlling the growth, orientation, placement and handling of nanostructures and can be incorporated into devices.

1.2 Objectives and organization of the document

The main objectives of this thesis is to build a robust carbon nanotubes machine to grown uniform, vertical, longer single stranded carbon nanotubes and address the issues that exist due to variation in design, plasma inconsistency and irregularity of temperature. Next step is to find process parameters to grow consistent carbon nanotubes. Then finding a recipe to make nano-dots which acts a template to grow single stranded carbon nanotubes and growing vertical CNTs at deterministic location. The future work would be to make polymer pellets with embedded single stranded CNTs of specified geometry. Then these pellets with exposed CNTs are transplanted to specific locations, where it can be used as In-plane AFM probe for scanning a surface or integrated with a device for micro-fluidic, photonic and electronic transfer. The main objectives of this research are represented in figure 1.1.

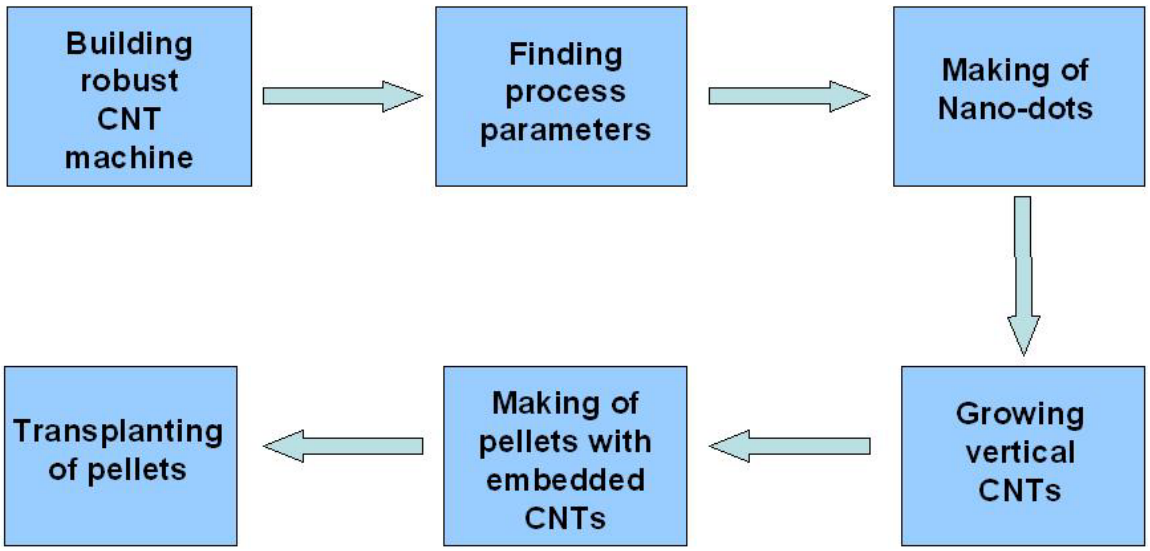


Figure 1-1 Main Objectives of this thesis

The document is organized to provide a comprehensive summary of the design, analysis, experimental methods and results involved in this research project. The first chapter reviews

the background, current practices and limitations to synthesis, handling, and functionalization of CNTs. The second chapter provides an insight of the development of nanopelleting concept and additive process flow for single stranded CNTs. The third chapter provides the detailed design, components used and procedure to use carbon nanotube machine. This chapter also deals with design of experiment to obtain optimized process conditions for growing carbon nanotubes. Fourth chapter presents the CNT growth results due to use of different gases and samples (patterned and un-patterned). Fifth chapter provides detailed design and analysis of CNT machine chucks to meet the specific requirements of the project. Sixth chapter provides an overview of making nickel nano-dot, growing single stranded CNT and address issues in making nickel nano-dot. The final chapter is a discussion of the results and areas for future investigation of nanopelleting concept and its applications.

1.3 Background

The nanopelleting process overcomes laborious steps to separate, handle, orient and cut to required length a single stranded CNT for any specific applications. Hence there is a need to establish as link between nanopelleting concept and synthesis, handling, functionalization of CNTs. This section gives an overview of properties of CNTs, nanotube growth reactors and current research practices to handle and assemble carbon nanotubes. Further, a brief comparison between nanopelleting concept and the current assemble technique found by other research groups.

1.3.1 Properties of carbon nanotubes

A SWCNT is composed of a rolled-up tubular shell of graphene sheet, which is made up of hexagonal rings of carbon atoms as shown in figure 1.2. A tube can roll up in many angles along the graphitic plane, effecting the crystal geometry and chirality of the tubes. There are two types of structures (a) an armchair CNT and (b) zig-zag CNT. The chirality or the orientations, is precisely defined by the exact twist of the honeycomb structure and in turn defines whether a CNT is a semiconductor or a conductor. A two-dimensional graphene sheet showing the chirality and TEM image of SWCNT is shown in figure 1.2 [13]. A MWCNT is composed of stack of graphene sheets rolled up into concentric cylinders, where walls of each layer are parallel to each other. The growth model of MWCNT is a four-step

process: 1) creation of a metal catalyst seed with a barrier layer; 2) decomposition of hydrocarbon source into carbon radical; 3) deposition of carbon onto the metal seed particle and 4) termination of the growth. J.G. Wen et al. [14] have proposed the growth mechanism and characterization of patterned metal catalyst (nickel) and uniform thin films to explain the phenomenon of diffusion and decomposition of carbon. During the growth of carbon nanotube a nickel particle sits at the tip of each tube (tip growth mode), and its [220] plane is orientated along the plasma direction, hence alignment of nanotubes is induced by the electric field direction relative to the substrate surface [14].

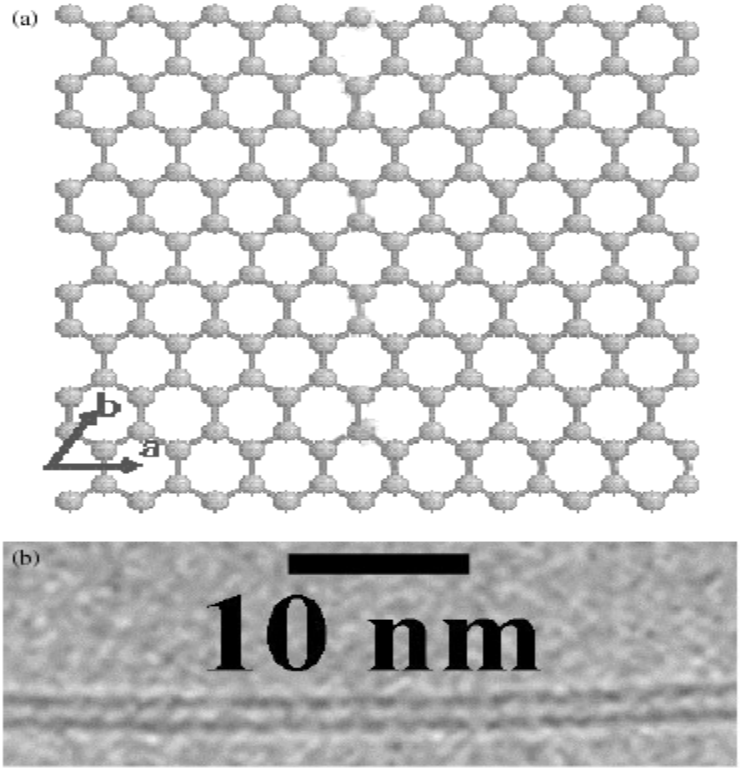


Figure 1-2 (a) Two-dimensional graphene sheet (b) TEM image of a SWCNT [13]

1.3.2 Growth methods

The three most widely used techniques used to grow carbon nanotubes are:

A) Arc Discharge

In an electric arc-discharge apparatus [6], the arc is generated between two electrodes in a reactor under a helium atmosphere. The cathode is graphite rod and the anode was also a graphite rod in which a hole is drilled and filled with a mixture of a metallic catalyst and graphite powder. The arc discharge was created by a current between the electrodes, where

carbon atoms are evaporated by plasma of helium gas ignited by high currents passed through opposing carbon anode and cathode. The electric-arc technique generates fullerenes and multiwalled and can generate large quantities of SWNTs. The advantage of this technique is: due to high growth temperature, the crystallinity and perfection of arc-produced CNTs are generally high, and the yield per unit time is higher than other methods. The disadvantage of this technique is: it is hard to grow aligned CNTs by arc discharge, although partial alignment of SWNTs can be achieved by convection or directed arc plasma.

B) Laser Ablation

This technique is used to produce fullerenes, metallofullerenes, SWNTs and multiwalled nanotubes. A scanning laser beam, controlled by a motor-driven total reflector is focused to a 6-7 mm diameter spot onto a metal-graphite composite target [7]. The method utilizes intense laser pulses to ablate a carbon target containing 0.5 atomic percent of nickel and cobalt. The target is placed in a tube-furnace heated to 1200ºC. During laser ablation, a flow of inert gas is passed through the growth chamber to carry the grown nanotubes downstream to be collected on a cold finger. The advantages of this technique are: high-quality SWNT production, diameter control, investigation of growth dynamics and the production of new materials.

C) Chemical Vapor Deposition (CVD)

The growth process involves heating a catalyst material to high temperatures in a tube furnace and flowing a hydrocarbon gas through the tube reactor for a period time. Materials grown over the catalyst are collected upon cooling the system to room temperature. The key parameters in nanotube CVD growth are the hydrocarbons (acetylene, methane), catalysts (Ni, Co, Fe), dilution gases (ammonia, hydrogen, nitrogen) and growth temperature. The critical steps involved in this technique are decomposition, diffusion and accumulation as represented in figure 1.3. The advantages of this technique compared with arc-discharge and laser methods are: CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure; more straight way to scale up production to industrial levels and allow more control over morphology and structure of the produced nanotubes. Plasma-enhanced type of CVD is most often used to obtain well-aligned MWCNTs at temperatures below 700º on many different substrates, including, silicon, glass and plastic

[14,15,16]. PECVD technique is used for the nanopelleting concept, since bulk (carpet) CNTs as well as individual CNTs with controlled location and density [17,18] is obtained. The key component used in a PECVD system is its inherent electric field (plasma) that aids alignment of growing CNTs. A variety of plasma sources for CNT growth are available: DC plasma, hot-filament aided with dc, RF source, microwave, inductively coupled plasma reactors and RF with magnetic enhancement. The DC plasma reactor has a simple design and growth mechanism of CNTs is optimal. The dc plasma reactor consists of a pair of electrodes in a grounded chamber with one electrode grounded and the other connected to a power supply. The negative dc bias voltage applied to the cathode dissociates the feedstock gas and generates many carbon-bearing radicals for carbon nanotube growth. The details of PECVD system are discussed in subsequent chapter of this thesis.

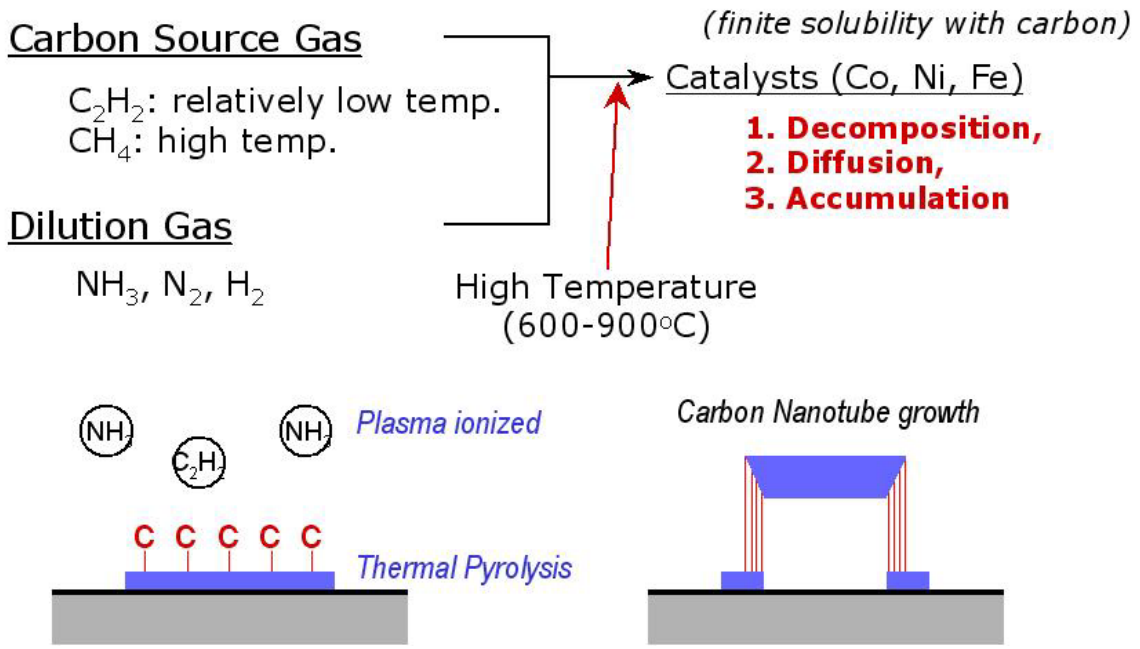


Figure 1-3: Growth of MWCNTs by CVD technique

1.3.3 Handling and assembly of carbon nanotubes

The current literature provides no insight for deterministic handling of CNTs to assemble in large-scale. Many research groups have attempted to handle CNTs by means like: Wei et al. [19] have tried growing CNTs across electrodes in circuits, Huang et al. [20] have used micro-fluidic channels flow to control the growth of nano-wires and Jung et al. [21] have grown CNTs across the posts formed on the substrate. Most of the current assemble

practices are done manually or by self-assemble. Self-assemble of CNTs involve the use of dispersed CNT solutions that are then selectively adhered to a patterned surface. Oh et al. [22] used self-assemble technique of SWCNTs for field-emission applications. In this paper purified SWCNTs bundles in suspension were assembled on the water-substrate-air triple line on pre-patterned substrates at room temperature. Rao et al. [23] used polar molecular patterning for self-assembly of SWCNTs. Individual polar molecule marks attract and align SWCNTs along pre-determined lines without external force, enabling any SWCNT-based structure to be assembled simply by using polar molecular patterns with the required shapes. Self assemble technique provides basic bulk handling of CNTs, but it does not provide a deterministic handling of individual CNTs or alignment of CNTs. In general of assemble of CNTs is divided into categories, serial and parallel assembly. Characteristics, advantages, disadvantages and examples of serial and parallel assembly are listed in table 1.1. The main examples of serial assembly are: direct contact with SPM tips, microtweezers and four point probes, soldering, shadow masking and examples of parallel assemble are: Dielectrophoresis and In-situ growth. Hence from above literature review and table it shows that there is a need for parallel and deterministic assembly of CNTs. The use of nanopellets enables a micro-scale parallel assembles for creating large-scale arrays of nanostructures.

Table 1.1: Serial and parallel assembly of CNTs

	Serial	Parallel
Characteristics	- Direct assembly - Mechanical tools directly touch and manipulate the nano-components	- Indirect assembly - Use electrical fields or in-situ growth to position the nano-components
Advantages	- Ideal for learning more about the components and building prototypes - Laboratory use	- good for large-scale integration
Disadvantages	- Slow	- Large variations
Examples	- Direct contact with SPM tips, microtweezers and four point probes - Soldering - Shadow masking	- Dielectrophoresis - In-situ growth

1.3.4 Functionalization of carbon nanotubes

Functionalization of CNTs refers to purification of CNTs, adherence to a surface, intercalation and chemical modification of the CNT structure. S. Banerjee et al. [24] have described a variety of molecular organic- and inorganic-inspired methodologies to chemically modify nanotube structures, including metal coordination, solution-phase ozonolysis, and the formation of nanotube-nanocrystal heterostructures. Chemical modifications of CNTs have implications for molecular electronics, photocatalysis and for scanning probe microscopy with fictionalized tips. CNTs are also functionalized with carboxyl or other groups for adhesion to a substrate as part of an assembly method. A large amount of research work has been done to connect and anchor CNTs. I. Kiricsi et al. [25] have demonstrated a unique method of connecting two CNTs. This is done by, depositing catalyst material on the outer surface of carbon nanotubes. The branches of nanotubes were produced at this contact point by catalytic chemical vapor deposition (CCVD) of acetylene. A. Bachtold et al. [26] have demonstrated logic circuits with field-effect transistors based on single carbon nanotubes. CNT is bridged (anchored) across two gates which acts as nanotube transistor and CNT is solder onto silicon by depositing gold. This nanotube transistor has a gate consisting of a micro-fabricated Al wire with a well-insulated native aluminum oxide layer, which lies beneath a semi-conducting nanotube that is electrically contacted to two gold electrodes.

CHAPTER 2

NANOPELLETING PROCESS

2.1 Concept of Nanopelleting process

In the previous chapter, various assembly and handling of nanostructures (CNTs) were discussed. These assembly efforts for nanostructures (such as carbon nanotubes) are mostly based on the concept of planting seeds and growing them into nanostructures, which cannot integrate nanostructures to micro/macro structures deterministically in a long-range order. So to overcome the problem of assembly at nanoscale, the nanopelleting concept was devised as a potential manufacturing process for CNTs by Professor Sang Gook Kim at MIT. This process is termed as nanopelleting, which refers to control length, alignment, handling and transportation of a nanostructure (carbon nanotube). This process has benefits in all the categories mentioned above. A PECVD machine is used to produce CNTs with controllable alignment and provides a mechanism to mechanically control the length. A polymer pellet of size 50-100 micrometer is used for shifting nanostructure to micro scale, allowing deterministic micro-scale handling and assembly. In terms of functionalization, the ex situ growth decouples the growth and use, providing higher yield of pellets which can be assembled over large areas. Thus nanopelleting process is a useful tool, where CNTs are grown using optimal conditions, modified as necessary and then assembled over larger areas for easy handling.

2.2 Process flows

A microelectronics fabrication work plan is created to produce nickel catalyst, CNTs (carpet or single stranded CNTs) and pellet economically and in less duration of time. There exists two possible process flows: a subtractive process that utilizes silicon trenches as molds for pellets and an additive process that involves creating pellets onto the substrate.

Subtractive process involves etching of the silicon substrate (to create molds where the pellet blocks can be cast), patterning at the bottom of each trench (titanium and nickel are deposited), growing carbon nanotubes, filling of trenches (SU-8 polymer is used), planarization of the filled pellets (CMP tool is used), releasing the pellets from the substrate

(silicon is etched) and transferring of pellets to a receptor substrate. This process is not economical and is time consuming, so additive process is used to make pellets. Benefits of additive process are there is no need of etching of silicon to create a mold and there is no need for mechanical polishing (CMP step is avoided) of the substrate. In additive process CNTs are grown on flat substrate and subsequently coated with a polymer, simplifying the patterning of the catalyst patches and reducing the number of process steps as compared to subtractive process. To prove this concept (additive process) a large area is used since it's easy to grow carpet of CNTs as compared to growing of single stranded CNTs.

2.2.1 Additive process flow for carpet of CNTs

Silicon wafer is used as a substrate to build up the pellet. First, a layer of titanium (15-25nm thick) is deposited which acts as a buffer layer and then a layer of nickel (15nm thick) is deposited. Carbon nanotubes are grown in CNT machine by using optimized process conditions. SU-8 is spin coated on silicon substrate containing carbon nanotubes and then exposed to UV light and developed to create pellets. SU-8 is epoxy based photoresist designed for micromachining and other MEMS applications. SU-8 is best suited for imaging near vertical sidewalls in thick films producing high aspect ratio structures, it has good coating properties (uniformity and adhesion), it dries faster and has higher throughput. Later these SU-8 pellets are released manually or by etching the silicon. Figure 2.1 shows the additive process flow for carpet of CNTs.

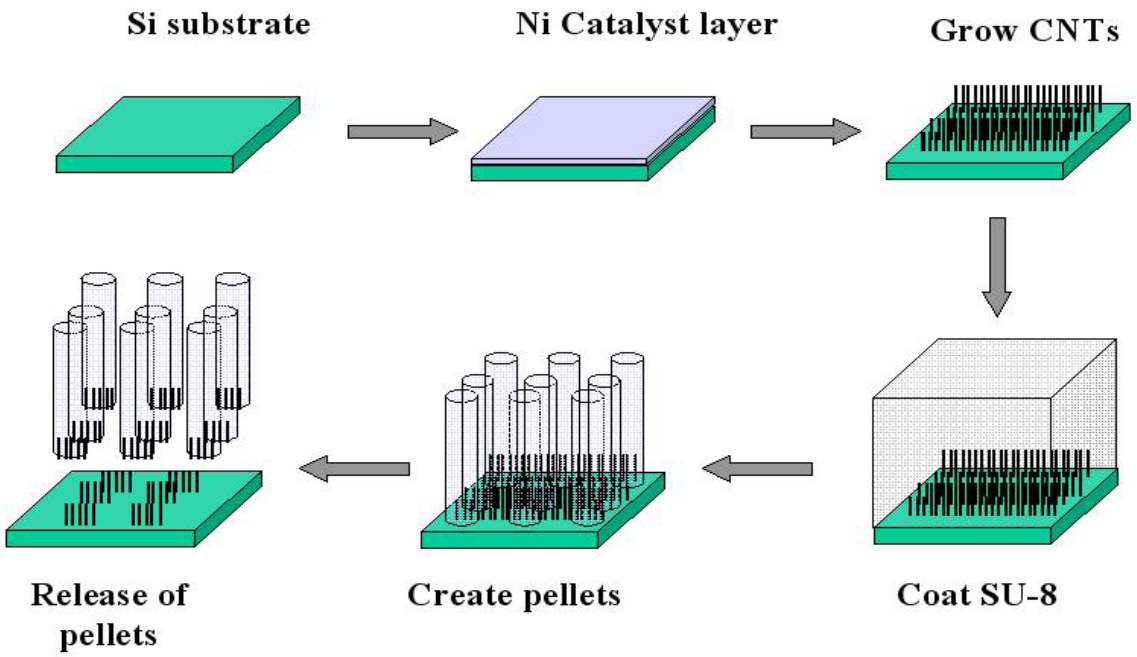


Figure 2-1: Concept of additive process flow for carpet of CNTs

Figure 2.2 shows micro-pellets formed with carpet of CNTs. First, 25nm thick titanium and 15nm thick nickel layers are deposited on a silicon wafer using e-beam deposition. Later uniform, vertical and longer CNTs are grown using proper process conditions inside the CNT machine. The process conditions used to grow CNTs as shown in figure 2.2 are: acetylene flow rate is 40sccm, ammonia flow rate is 160sccm, pressure inside the chamber is 8 Torr, temperature of the substrate is 550-562 C, plasma voltage is around 500-510V, growth time is 10 minutes and the power used is around 266-290 Watts. Carbon nanotubes are grown by nucleation of nickel and dissociation of acetylene gas (generates many carbon-bearing radicals). Following steps are used to make 25 micrometer thick and 15 micrometer diameter pellets: SU-8 2025 is coated at 2000 rpm spin speed, pre-baked at 65° C for 2 minutes, soft baked 95° C for 5 minutes, exposed using UV light and then developed using PM Acetate. Figure 2.2 shows arrays of micro-pellets and a single pellet containing carbon nanotubes.

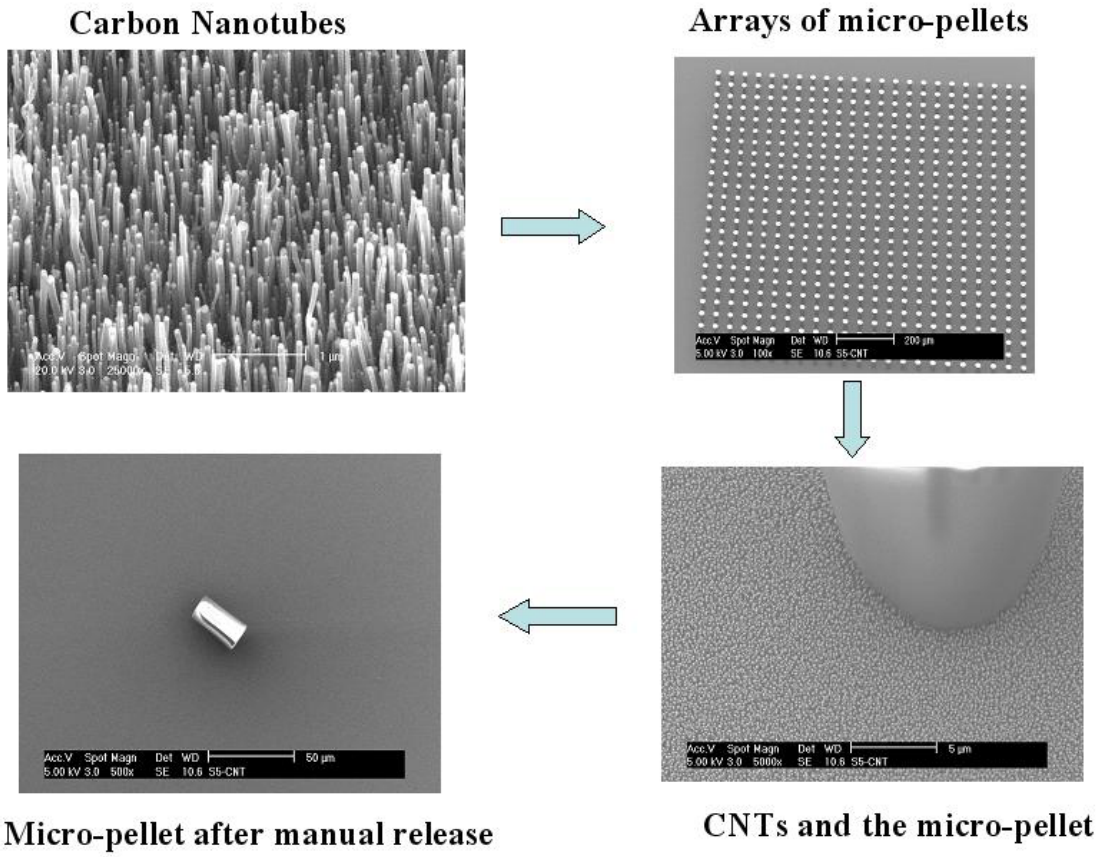


Figure 2-2: Micro-pellets with carpet of CNTs

2.2.2 Additive process flow for single stranded CNTs

Figure 2.2 shows that additive process works for carpet of CNTs, so our objective is to make pellets with single stranded CNT. The additive process flow for single stranded CNT is shown in figure 2.3. Important steps involved in this process are making of nickel catalyst nano dots, placing the nickel nano-dots in deterministic location, growing of single stranded CNTs using optimized process conditions, making of SU-8 pellets and releasing of these pellets. Making of nickel nano-dots and placing them in deterministic locations is done by using scanning electron beam lithography, which enables the writing of patterns of arbitrary geometries with minimum features as fine as 17 nm. A detailed recipe of making nickel nano-dots and growing of single stranded CNTs is discussed in chapter 5. SU-8 Pellets containing single stranded CNTs are made by the same recipe as micro-pellets with carpet of CNTs. Later these SU-8 pellets are released manually or by etching the silicon.

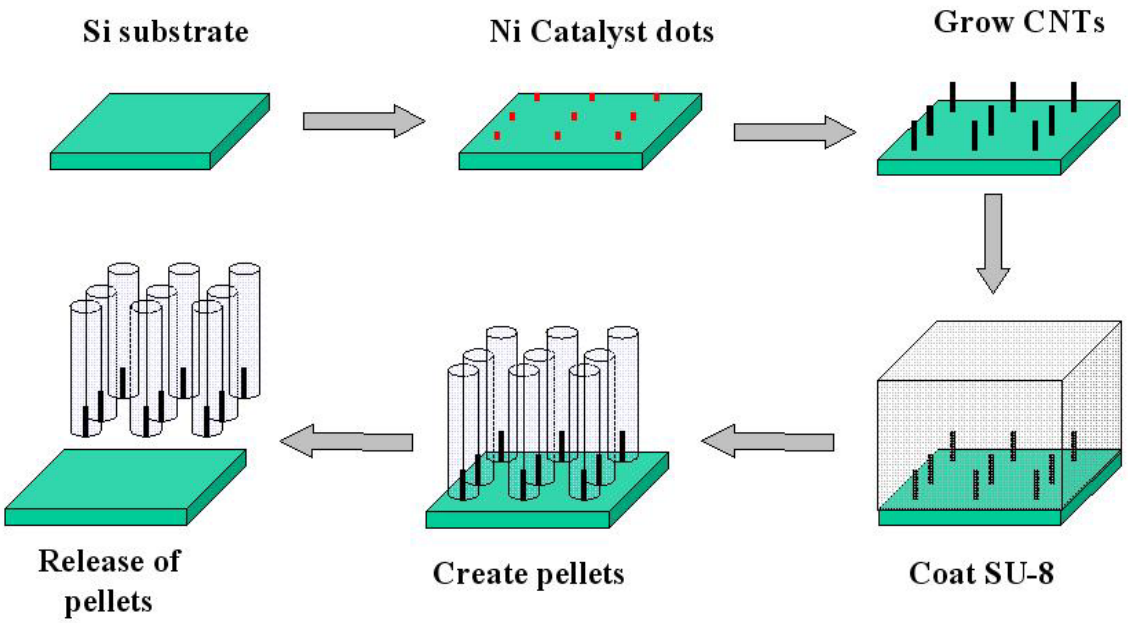


Figure 2-3: Concept of additive process flow for Single Stranded CNTs

CHAPTER 3

PECVD CNT GROWHT MACHINE

3.1 Design of the machine

CNTs are grown vertically, both individually and in bunches on the patterned metal catalyst using PECVD machine built by us at MIT (Figure 3-1a). Among various CNTs growing methods such as arc discharge, pyrolysis, laser vaporization, thermal CVD, plasma enhanced CVD has received considerable attention because PECVD can grow vertically aligned CNTs at a relatively low temperature with a high yield. A variety of plasma sources for CNT growth are available: DC plasma, hot-filament aided with dc, RF source, microwave, inductively coupled plasma reactors and RF with magnetic enhancement. We have built a DC plasma reactor because the design of the machine is simple and growth mechanism of CNTs is optimal. The dc plasma reactor consists of a pair of electrodes in a grounded chamber with one electrode grounded and the other connected to a power supply. The negative dc bias voltage applied to the cathode dissociates the feedstock gas and generates many carbon-bearing radicals for carbon nanotube growth. We are now running this PECVD machine at the MIT's Exploratory Materials Laboratory (EML), a class 1000 clean room, to find out the optimum process conditions to grow vertically aligned CNTs.

(a) (b)

Figure 3-1: (a) MIT CNT growing PECVD (b) In-side the vacuum chamber

3.2 Components of PECVD machine

The machine built has the following parts: Rotary pump to obtain a pressure of 10^{-2} Torr, Turomolecular pump to obtain a pressure of 10^{-6} Torr, Vacuum chamber to with-stand high temperature, MFC to measure the flow of acetylene and ammonia gas, vacuum gage to sense the pressure, plasma power supply to ignite plasma, ceramic ring to protect the cathode, ceramic heater to obtain a temperature up to 800°C, heater controller to vary the temperature and tube fittings for flammable and toxic gases and water flow (as shown in Figure 3-1a). Components of CNT machine and their uses are listed in Table 3-1. At the bottom of the ceramic heater three thermocouples are connected to measure the temperature, which is controlled by the heater controller as shown in figure 3-1b. Plasma is formed between anode and cathode by applying a DC voltage and ions formed by ammonia and acetylene gases as shown in Figure 3-1b. Acetylene then decomposes into carbon which deposits below the Ni catalyst and leads to the formation of carbon nanotubes.

Table 3-1: Components of Carbon nanotube machine and uses

Components	Uses
Rotary pump	Pressure of 10^{-2} Torr
Turbomolecular pump	Pressure of 10^{-6} Torr
Chamber and body	With-stand high temperature
MFC's	Measure the flow of CH4 and NH3
Vacuum gage	sense the pressure
Plasma power	To ignite plasma
Ceramic heater	Temp. of 800°C
Heater controller	To Vary the temperature
Tube Fitting	For gas and water flow

The machine uses the plasma sheath to orient the CNT growth thus resulting in the production of vertical structures. It uses acetylene as the C source and ammonia as etch back gas, and can use a number of CNT seeds such as nickel, molybdenum, and iron. The machine normally operates in the 550 – 650 °C range, and can process substrates up to 4" of diameter, with active area up to 2" of diameter, with the single electrode configuration.

3.3 Procedure for using the CNT machine

3.3.1 Loading samples

1. Vent the plasma chamber with nitrogen until atmospheric pressure is reached, using the nitrogen-purging valve. When the filling process is finished, the chamber will over pressurize, and nitrogen (N2) will start blowing out of the chamber base. Close N2-venting valve when finished.
2. Push the Hoist button once to open the plasma chamber. Wait until the mechanical system is fully opened before proceeding.
3. Load your samples on the wafer chuck. center the active area of your substrate with respect to the wafer chuck center. The CNT chuck holds both pieces and complete

wafers.

4. Push the Hoist button to close the plasma chamber. Make sure that the o-ring of the plasma chamber hull has a clean surface to seal against. Perhaps, wipe clean with an IPA wetted fabwipe.

3.3.2 Making vacuum before deposition

1. Open the Gate Valve and pump down to 100 Torr.

2. Do two N2 vent purges, performing the following procedure:

   i. Open the nitrogen-venting valve until the chamber pressure reaches 200 Torr.

   ii. Close the N2-venting valve, and let the plasma chamber pressure drop to 100 Torr.

   iii. Repeat the sequence one more time to complete the second purge; then, continue pumping out the chamber.

3. Once the plasma chamber is below 0.6 Torr, you can activate the turbo molecular pump. Push the Start button 4"x4" turbo controller panel. Then, wait approximately for 1.5 hours until the plasma chamber pressure goes down to 1×10^{-6} Torr.

3.3.3 Raising substrate temperature

1. Start the flow of cooling water. To do this, open the two yellow valves for water that are placed on the wall behind the CNT.

2. Disconnect the ionization vacuum gage before gas flow-in by moving the ion gage switch to the OFF position.

3. Turn ON the power of the heater controller, which is located at the bottom of the control panel.

4. Set the temperature of the zone 1 controller by holding the up button (▲). The temperature for CNT growth falls in the 550 – 650 °C range, but it is required to ramp up in two stages as the ceramic heater can break if heated or cooled too rapidly:

   i. First, Increase the temperature to 300 °C, and allow temp to stabilize.

   ii. Then, increase the temperature to your target temperature. This will take about 30 minutes.

5. Depending on the size of sample, you can use the zone 2 controller. For example, substrates with active areas that don't fall inside a central circle of 2" of diameter require zone 2 heating. If zone 2 is needed, reach the target temperature of zone 2 with the

same ramp up procedure that was described to the zone 1 controller.

6. Open the Turbo N2 purge (this prevents corrosives from going into the turbo bearings, and is different from the chamber N2 purge/vent).

3.3.4 Preparing gas flows and chamber run pressure

1. Make the reacting gases available to the plasma chamber. To do this, turn the three yellow valves and the tank valve of the gas tank cabinet that supplies ammonia. Also, turn the two yellow valves and the tank valve of the gas cabinet that supplies acetylene. Flip over the "closed" labels on both gas cabinets to re-label them as "open".

2. Turn on the MFC controller power switch.

3. Set the flow rates of acetylene (channel 1) and ammonia (channel 2). There is an On/Off switch for each gas, as well as for two unused MFC channels, and there is a dial to view the flow rate of one of these at a time. The flow rate can be adjusted by turning the set point screw and watching the change in actual flow if the dial is set to the correct channel.

   i. Select display channel 2 without turning on the switch for Channel 2 (the ammonia should not be flowing). Set the flow rate value of ammonia by pushing up the set point switch of channel 2 and, at the same time, turning the potentiometer on the right of the set point 2 with a screwdriver. A recommended starting value is 160 sccm.

   ii. Select display channel 1 without turning on the switch for channel 1 (the acetylene should not be flowing). Set the flow rate value of acetylene by pushing up the set point switch of channel 1 and, at the same time, turning the potentiometer on the right of the set point with a screwdriver. The recommended starting value is 40 sccm.

4. Turn on the channel 2 switch to start the flow of ammonia. Set chamber pressure by partially closing the gate valve while inlet gas is flowing. Adjust to about 8 Torr. Wait until the temperature stabilizes at the target temperature. Ammonia etches the CNT seed, and we know that in this machine a 15 nm thick Nickel seed disappears after about 30 minutes of ammonia flow without the presence of acetylene. For films 15 nm Ni films, do not flow the ammonia without flowing acetylene for more than about 15 minutes.

5. Quickly turn on Acetylene, channel 1, which should be at the correct flow rate already, and adjust the gate valve to reach 8 Torr. The temperature should not substantially change, as the acetylene flow rate is smaller than the ammonia flow rate.

3.3.5 Deposition

1.Turn the dc plasma supply ON. The output should be in OFF, the current should be in ON. Current and voltage indicators should be in 0.0

2. Turn on the output switch. Then, gradually rotate the Power level knob clockwise, observing the input voltage (current or power) increase, until plasma ignites, which usually occurs at about 500 V. As a reference, the plasma should be bluish.

3. Start the deposition timer. Under some conditions, 10 minutes is enough to grow CNTs 2 microns long.

4. After process time is over, turn off the plasma power. To do this,

i. Rotate the Power level knob counter-clockwise, until no voltage is biased to the plasma.

ii. Then, turn off the output.

iii. Finally, turn off the Plasma power.

5. Turn off the MFCs by setting OFF Channel 1 and Channel 2. Turn off the Main MFC switch.

6. Set the zone 1 (and zone 2 if used) heater value to 15 °C. Turn off the Heater Controller main switch, to allow the heater to cool down slowly so its ceramic elements don't break.

3.3.6 Sample unloading

1. Close the three yellow valves and the tank valve of the ammonia, and the two yellow valves and the tank valve of the acetylene, and flip over the "open" labels on both gas cabinets to re-label them as "closed".

2. Open fully the gate valve for 30 minutes.

3. After 30 min, turn off the turbo by pushing the start button on the turbo panel, and turn off the turbo N2 purge

4. Carry out three nitrogen purges, performing the following procedure.

i. Open the N2-vent valve until the plasma chamber pressure rises to 200 Torr.

ii. Then, close the nitrogen-venting valve, and let the plasma chamber pressure drop to 100 Torr.

iii. Repeat the sequence two more times to complete the purge series.

5. Fully close gate valve.

6. Open the N2 vent, until the chamber is over pressurized and starts venting excess N2.

7. Push the Hoist button to open the plasma chamber, and turn off N2 vent. Wait until the mechanical system fully lifts the plasma chamber hull.

8. Remove your samples from the wafer chuck with dedicated tweezers and store in compatible locations.

3.4 Design of experiments for CNT growth

We use methane (acetylene) gas as a carbon feeding gas and ammonia as a dilution gas. The ratio between two gases affects the quality of CNTs. And also, heating temperature, growth time, and plasma voltage affect the quality of CNTs. These factors should be properly adjusted to make straight and vertically aligned CNTs. In this research, we would like to use the design of experiments method with orthogonal array to minimize the number of runs to reach the optimum process condition. Generally, the design of experiments method is an effective method in improving product reliability and reducing costs. Therefore, systematic approach using design of experiments method to find the optimum CNT process condition will not only reduce costs but also guarantee good quality of CNTs even if environmental noise factors. The best combination of control factors for straight and vertically aligned CNTs will be searched by using design of experiments method with orthogonal array.

3.4.1 Control factors and figure of merit

Three control factors, CH_4/NH_3 gas ratio, heating temperature, and growth time are selected for the first orthogonal array. Each factor is classified into 3 levels. We would like to carry out 9 experiments by using a L9 orthogonal array to find out the best combination. If we use the full factorial experiment method, 27 runs will be required. The figure of merit (FOM) is defined as the multiplied value of three functional requirements. In defining FOM, we used the multiplication of three values instead of the summation. The reason is to assign relatively high score to sample, which are satisfactory in all functional requirements. The functional requirements of CNTs are uniformity (Y1), perpendicularity (Y2), height (Y3), and diameter

consistency (Y4). The diameter consistency is omitted in calculating FOM. Because diameter consistency level of whole SEM pictures are satisfactory and it is hard to find pyramidal shape CNTs from SEM pictures. Nine SEM pictures are sorted in order of good uniformity for Y1. 9 point is given to the best uniformity SEM picture and 0.5 point is given to the worst uniformity SEM picture. If it's hard to distinguish uniformity difference between two samples, the same points are given. For Y2 and Y3, the same rule is applied. Figures 3-2, 3-3 and 3-4 show SEM pictures that are sorted in order of each functional requirement (uniformity, perpendicularity and height).

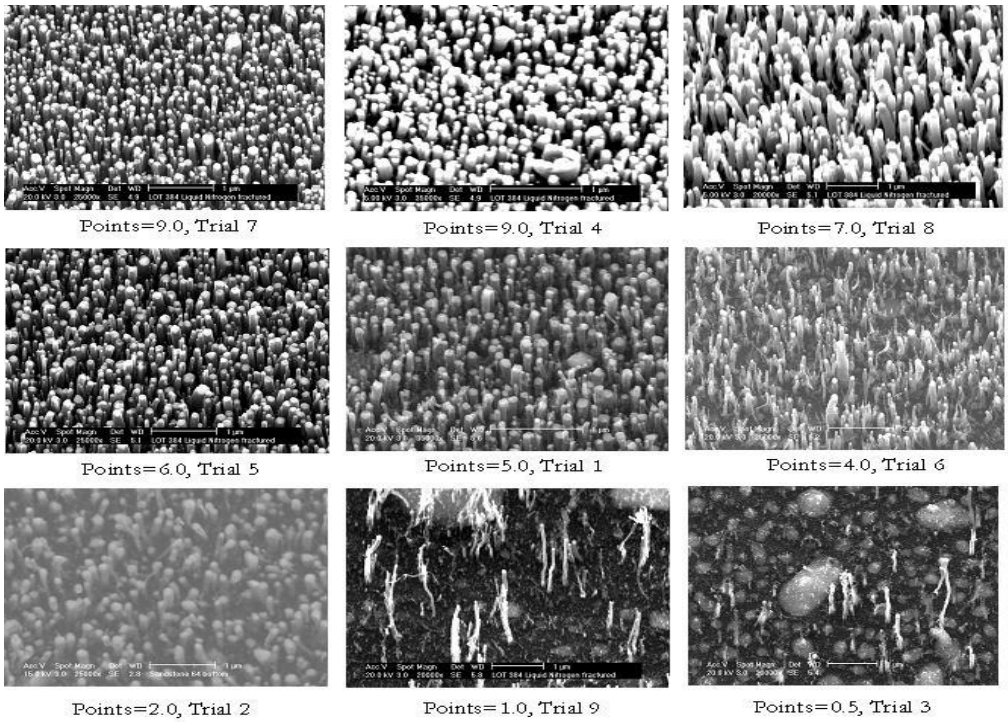


Figure 3-2: SEM pictures in order of good uniformity (Y1)

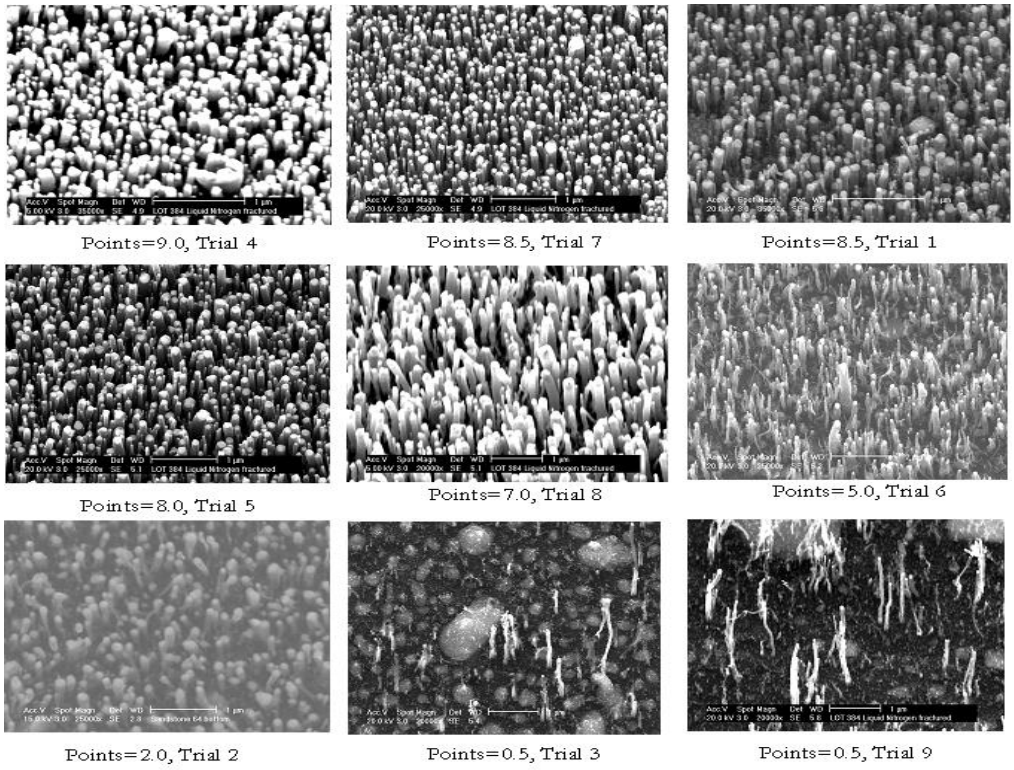


Figure 3-3: SEM pictures in order of perpendicularity (Y2)

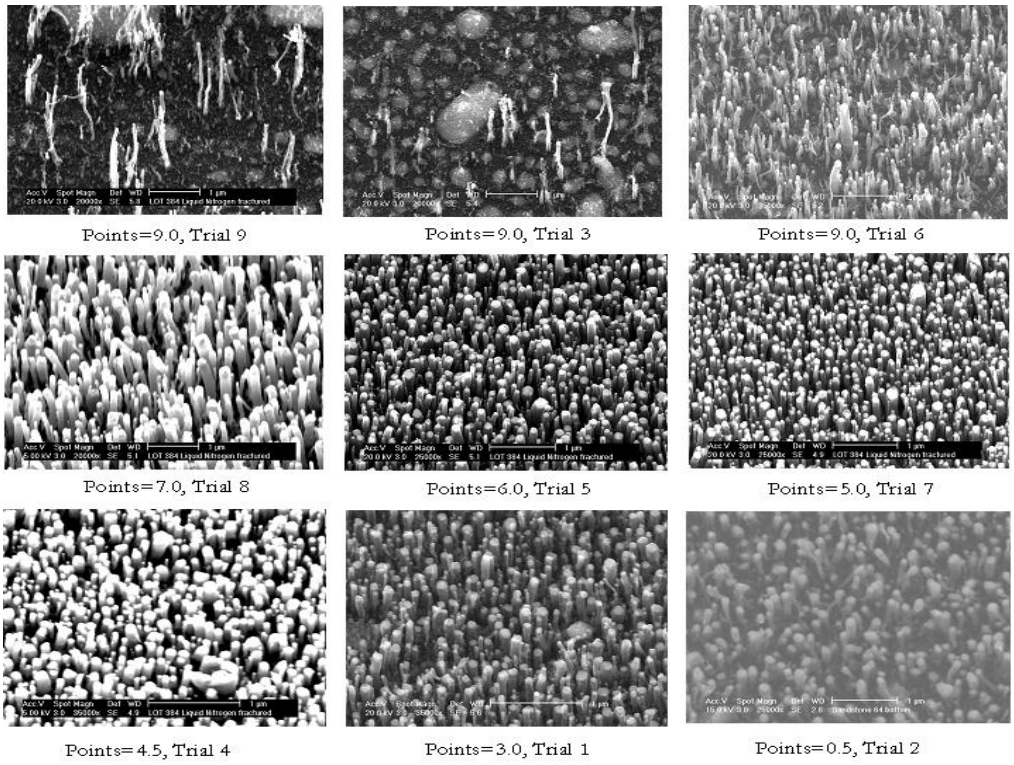


Figure 3-4: SEM pictures in order of height (Y3)

3.4.2 Results and analysis

Table 3-2 shows the experiments trial table for CNT growth condition search. Three control factors used for these experiments are gas ratio, heat temperature and growth time. Figure 3-5 shows the main effect of each factor. The FOM value (y_{ijk}) is computed by the equation (3-1) as shown in below. If we select gas ratio in level 1 (33.33%), the estimated FOM value will be decreased. But it will be increased if we select gas ratio in level 2 (66.66%) or level 3 (50.00%). From this result, we can find that higher gas ratio and lower temperature is desirable for good quality CNTs. In this stage, the exact value of FOM is not important because that are given subjectively. In the case of growth time, level 1 (15 min) and level 3 (20 min) shows almost same result. Therefore, we should avoid growth time of 10 minutes (level 2).

Table 3-2: Experiments table for CNT growth condition search

Trial	Control Factors			Result			
	Gas ratio*	Heat Temp	Growth time	Y1	Y2	Y3	FOM
1 (S10)	33.33%	550 °C	15 min	5	8.5	3	127.5
2 (S14)	33.33%	600 °C	10 min	2	2	0.5	2.0
3 (S12)	33.33%	700 °C	20 min	0.5	0.5	9	2.25
4 (S24)	66.66%	550 °C	10 min	9	9	4.5	364.5
5 (S26)	66.66%	600 °C	20 min	6	8	6	288.0
6 (S28)	66.66%	700 °C	15 min	4	5	9	180.0
7 (S20)	50.00%	550 °C	20 min	9	8.5	5	382.5
8 (S18)	50.00%	600 °C	15 min	7	7	7	343
9 (S22)	50.00%	700 °C	10 min	1	0.5	9	4.5

* Gas ratio
33.33% : CH4- 80 sccm, NH3-160 sccm
66.66% : CH4- 200 sccm, NH3- 100 sccm
50.00% : CH4- 160 sccm, NH3- 160 sccm

- Y1: Uniformity
- Y2: Perpendicularity
- Y3: Height
- F.O.M : Y1*Y2*Y3

$$y_{ijk} = u + Gas_i + Temp_j + Time_k \quad (3\text{-}1)$$

where, $u = average$

Gas_i = contribution amount of factor Gas in i level to average

$Temp_j$ = contribution amount of factor Temp in j level to average

$Time_k$ = contribution amount of factor Time in k level to average

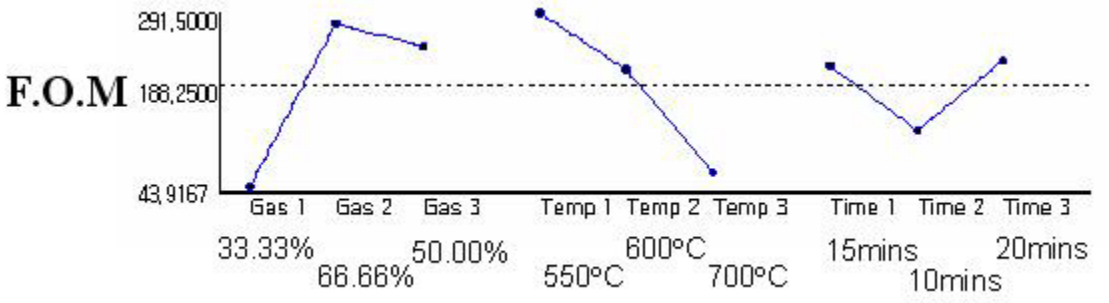


Figure 3-5: Main effect of each factor

From main effect analysis result, we can expect that the best combination of control factors is Gas level 2 (66.66%); Temperature level 1 (550 °C); Growth time level 3 (20 min).

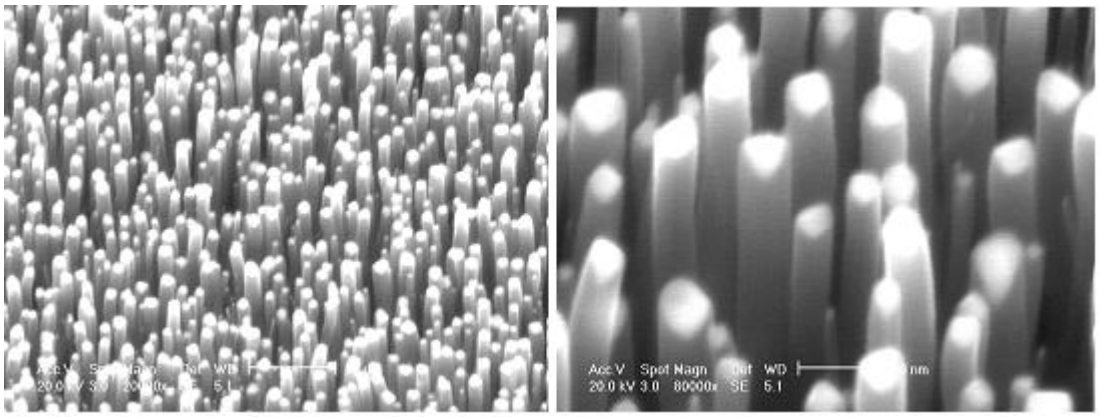


Figure 3-6: SEM pictures of CNTs grown by best combination

Figure 3-6 shows the SEM pictures of CNTs that was grown with the best combination of control factors in figure 3-5. The diameter of CNTs is about 150nm – 200nm. The reason of diameter change seems to be the plasma intensity change. The diameter uniformity and perpendicularity are satisfactory but the length of CNTs (≈ 1 μm) is not reached to our target length (5 μm). If we use acetylene gas as a carbon feeding gas instead of methane, it is expected to get 5 μm length vertically aligned straight CNTs. Furthermore, the design of experiments method using orthogonal array could be used efficiently in the case of acetylene gas.

CHAPTER 4

CNT GROWTH RESULTS

Carbon nanotube growth on catalyst (nickel) is similar to gas-solid interaction process where thin film deposits on a substrate. Hydrocarbons like methane, ethylene and acetylene are decomposed by plasma and adsorbed onto the catalytic surface, where carbon precipitates in a crystalline tubular form. Since the plasma and heat decomposes the hydrocarbon creating reactive ions, the use of pure hydrocarbon lead to undesirable amorphous carbon. Hence, there is a need to dilute the hydrocarbon with argon, hydrogen or ammonia gas. This chapter is focused on investigating the effects hydrocarbon (methane or acetylene) on nanotubes growth rate, diameter, density, alignment and structure.

4.1 Use of Methane gas

The optimized process condition for CNTs grown (using methane gas) is obtained by carrying out nine experiments using orthogonal array as discussed in section 3.4. The sample is made of Si/Ti/Ni (Ti: 25nm, Ni: 25nm), growth time is 20 minutes, methane flow rate is 200sccm, ammonia flow rate is 100sccm, pressure inside the chamber is 8 Torr, temperature of the substrate is 550-600^{o} C, plasma voltage is around 500-510V and the power used is around 165-215 Watts. The length of the carbon nanotubes obtained were around 1-1.5 micrometers and the diameter of the tubes were around 100-150 nm as shown in Figure 4-1.

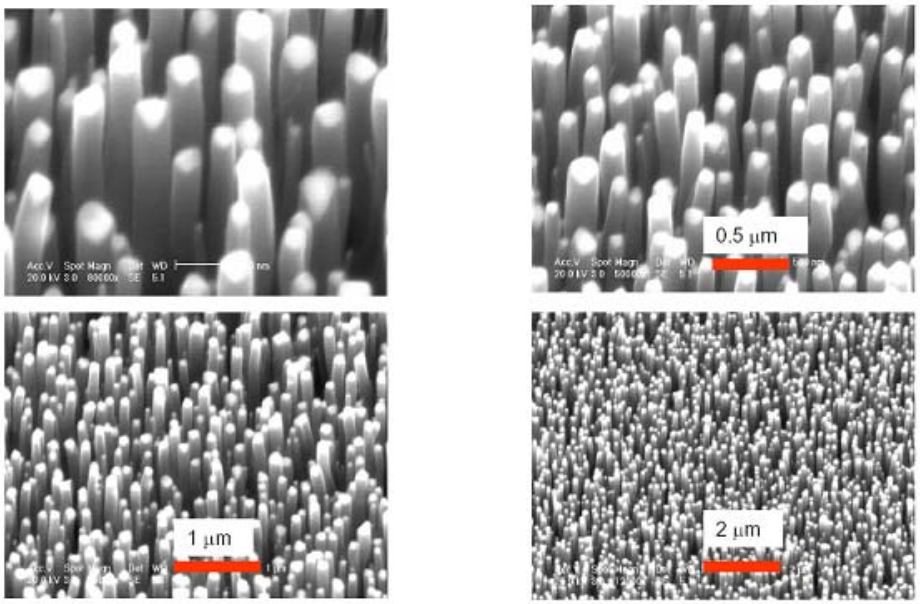


Figure 4-1: CNTs grown using methane gas

4.2 Use of Acetylene gas

The optimized process condition for CNTs grown (using acetylene gas) is obtained by carrying out nine experiments using orthogonal array as discussed in section 3.4. The sample is made of Si/Ti/Ni (Ti: 25nm, Ni: 25nm), growth time is 10 minutes, acetylene flow rate is 40sccm, ammonia flow rate is 160sccm, pressure inside the chamber is 8 Torr, temperature of the substrate is 550° C, plasma voltage is around 500-510V and the power used is around 266-290 Watts. The length of the carbon nanotubes obtained were around 1.5-2 micrometers and the diameter of the tubes were around 50-100 nm as shown in Figure 4-2.

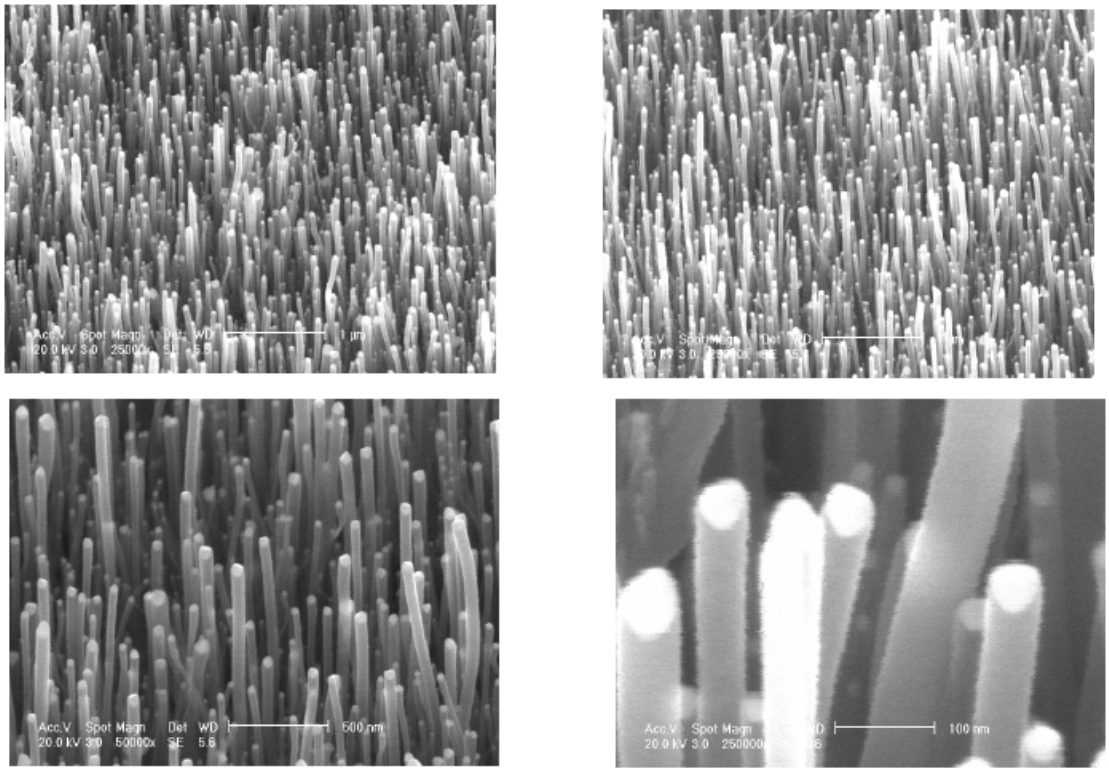


Figure 4-2: CNTs grown using acetylene gas

4.3 CNT growth with Acetylene gas in the trenches

To create trenches on silicon wafers following process are carried out: the wafer is spun by positive photo resist, pre-baked, exposed, developed and then post-baked. Silicon is etched using KOH and then photo resist is striped off. The process is repeated using a mask of desired pattern to deposit Ti and Ni and a lift off process is done at the end. Thus different sized Ni patches are formed in these trenches.

The optimized process conditions for CNTs grown as shown in Figure 4-3 are: the sample is made of Si/Ti/Ni (Ti: 25nm, Ni: 25nm), growth time is 10 minutes, acetylene flow rate is 40sccm, ammonia flow rate is 160sccm, pressure inside the chamber is 8 Torr, temperature of the substrate is 550-562 C, plasma voltage is around 500-510V and the power used is around 266-290 Watts.

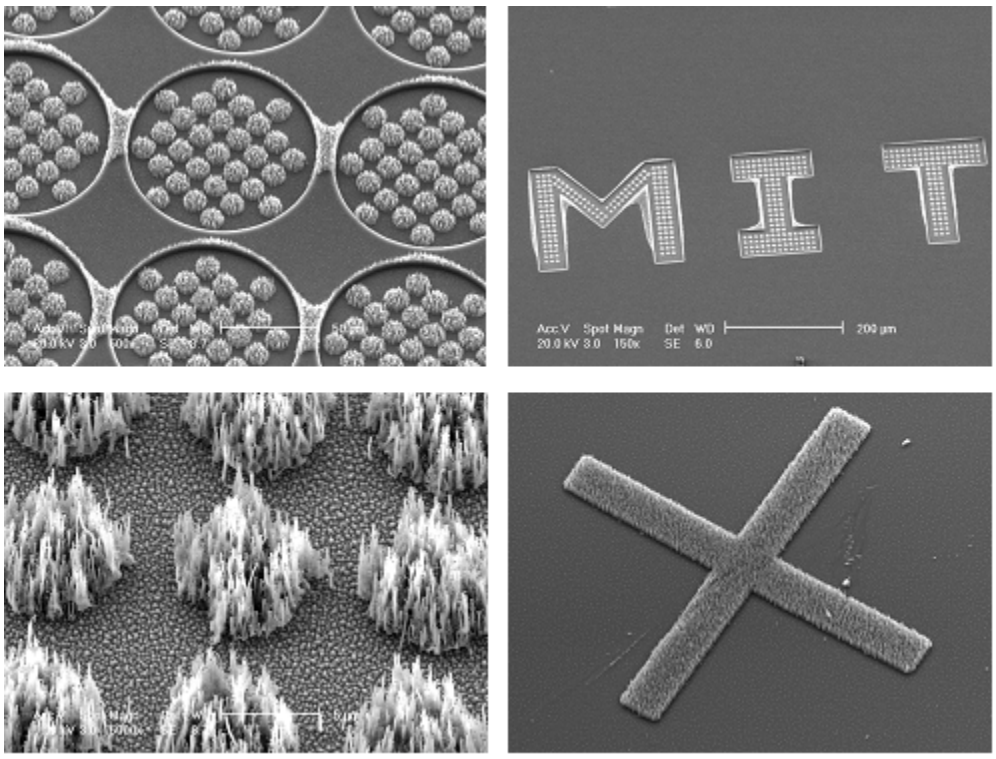
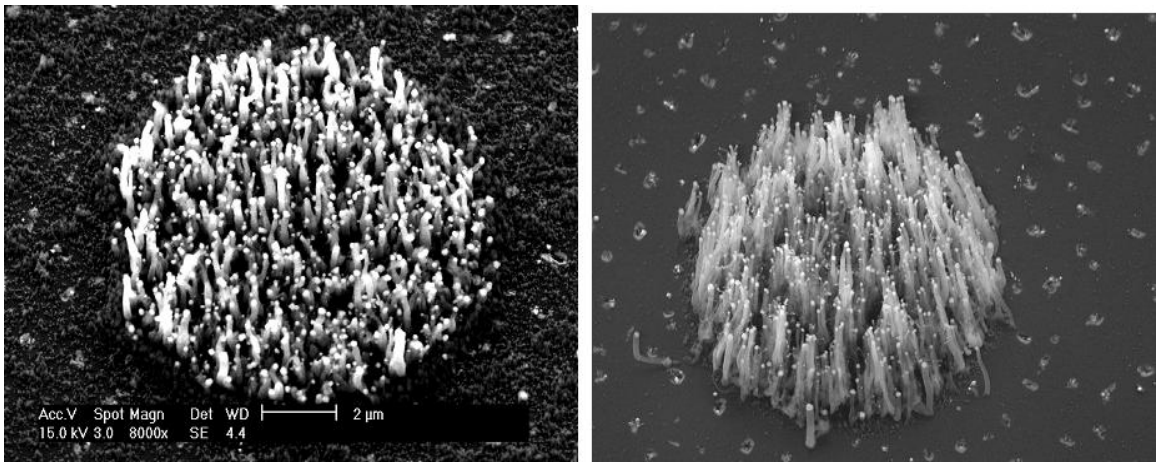


Figure 4-3: CNTs grown using acetylene gas in the trenches

4.4 Comparison of Using Methane and Acetylene gases

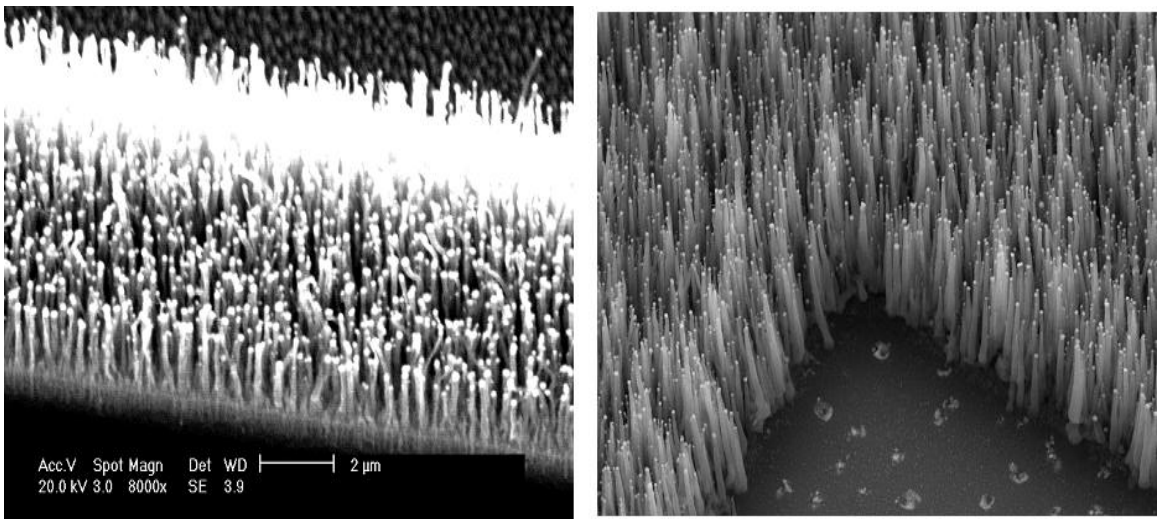
Patterned (5 micrometer Ni patched) and non-patterned (Ni film) samples are used for the comparison of growth mechanism for two different carbon gases. Methane gas absorbed onto the catalytic particle surface releases carbon upon decomposition at higher temperature compared to acetylene gas, which then dissolves and diffuses into the particle. The attachment of nickel particle to the surface of titanium is weak and the carbon precipitates at the bottom surface of the nickel particle and the filament lifts the particle as it grows. This is called as the tip growth model. Figure 4-1~5 shows tip growth mode since the nickel particle remains at the top during the growth of carbon nanotube. In figure 4-4 (a) the process conditions used for C_2H_4 gas are: Sample type: Patterns with NO trench Si/Ni/Ti (Ni: 25 nm, Ti: 25nm), Pressure: 8 Torrs, Methane: 80 sccm, Ammonia: 160 sccm, Growth Time: 20 min, Temperature: 600-614°C, Voltage: 503 Volts. The length of nanotubes was 1-2 micrometer. In figure 4-4 (b) the process conditions used for C_2H_2 gas are: Sample type: Patterns with NO trench Si/Ni/Ti (Ni: 25 nm, Ti: 25nm), Pressure: 8 Torrs, Acetylene: 40

sccm, Ammonia: 160 sccm, Growth Time: 15 min, Temperature: 600-614° C, Voltage: 503 Volts. The length of nanotubes was 2-5 micrometer.



(a) (b)

Figure 4-4: Comparison of CNTs grown on 5-micron Ni patch using (a) C_2H_4 gas and (b) C_2H_2 gas



(a) (b)

Figure 4-5: Comparison of CNTs grown on wider Ni film using (a) C_2H_4 gas and (b) C_2H_2 gas

In figure 4-5 (a) the process conditions used for C_2H_4 gas are: Sample Type: Patterns with trench Si/Ni/Ti (Ni: 25 nm, Ti: 25nm), Pressure: 8 Torrs, Methane: 80 sccm, Ammonia: 160 sccm, Growth Time: 20 min, Temperature: 600-614°C, Voltage: 503 Volts. The length of nanotubes was 1-2 micrometer. In figure 4-5 (b) the process conditions used for C_2H_2 gas are: Sample Type: Patterns with trench Si/Ni/Ti (Ni: 25 nm, Ti: 25nm), Pressure: 8 Torrs, Acetylene: 40 sccm, Ammonia: 160 sccm, Growth Time: 15 min, Temperature: 600-614° C, Voltage: 503 Volts. The length of nanotubes was 2-5 micrometer.

The advantages of using acetylene gas over methane as shown in figure 4-4~5 are: 1) time for growth of CNTs is reduced (10-15 minutes) to grow 2-5 micrometer; 2) temperature of growth is around 550-600° C; 3) uniformity is better; 4) perpendicularity is also good. The disadvantage of using acetylene gas is that, there is lateral growth below the metal cap which dominates as compared to vertical nanotube growth, hence giving rise to pyramidal structures (as shown in figure 4-4~5). This indicates that relative amount of ammonia in the plasma is less; the etching rate is lower than the deposition rate, resulting in amorphous carbon between the structures.

CHAPTER 5

CNT MACHINE: TEMPERATURE CONTROL

In a PECVD machine the most important part is the chuck, where the substrate is heated and plasma is formed. The understanding of plasma and substrate heating mechanism is critical because it effects the formation of catalytic nanoclusters and growing of well-aligned carbon nanotubes. The CNT chuck includes an external heating source, electrically isolated thermocouples to measure the temperature of heater, dc bias (anode, cathode) and the wafer holder. The CNT machine chuck is made electrically isolated (electrically floating) because any metal coming in contact acts as anode and leads to the formation of plasma or sparks in the region close to metal. So there is a need for uniform and consistent plasma to be formed above the wafer holder. This chapter discuss about different design and analysis of CNT machine chuck in order to obtain uniform temperature across the wafer and consistent plasma, which leads to formation of well-aligned, longer carbon nanotubes.

5.1 Design analysis of CNT machine chuck-1

The CNT growing PECVD machine as shown in figure 3-1 had a first chuck design as shown in figure 5-1. Chuck-1 had following parts: two-zone heater, ceramic insulator, metal support, metal posts, thermocouples and wiring for electrical connections. The heater used was Advanced GE heater with inner and outer zones with following specifications: resistance of inner coil is 18 ohms, resistance of outer coil is 20 ohms, diameter of heater is 100mm, maximum current is 13 A and thickness is 5mm. Four insulated copper wires are connected to the four legs of the heater for electrical connections. This heater is assembled inside a titanium container, where the top surface acts as a cathode. This heater assembly is held by an outer titanium support and a ceramic insulator is used to separate these two pieces. Insulated metallic posts support the chuck. Three thermocouples are fixed to the heater assembly from the bottom as shown in figure 5-1. These thermocouples are used the measure the temperatures of inner heater coil, outer heater coil and for over temperature.

A titanium rod, which is held by a support, is used as anode. The distance between anode and cathode is critical because it signifies the strength of the plasma field, which in turn affects the growth of carbon nanotues. There are two gas showers where ammonia and acetylene gases are passed and are placed above the anode so that uniform mixing takes place. The CNT machine chuck-1 gave good results as shown if figure 4-1~5, but it started drifting after prolonged use. This chuck design had following issues: inconsistent plasma, electric sparks at the bottom plate, carbon deposition on metal surfaces, lots of metal and ceramic parts (difficult to assemble and disassemble parts) and miss fit of thermocouples. Hence, a new design of chuck (chuck-2) was made to overcome some these limitations.

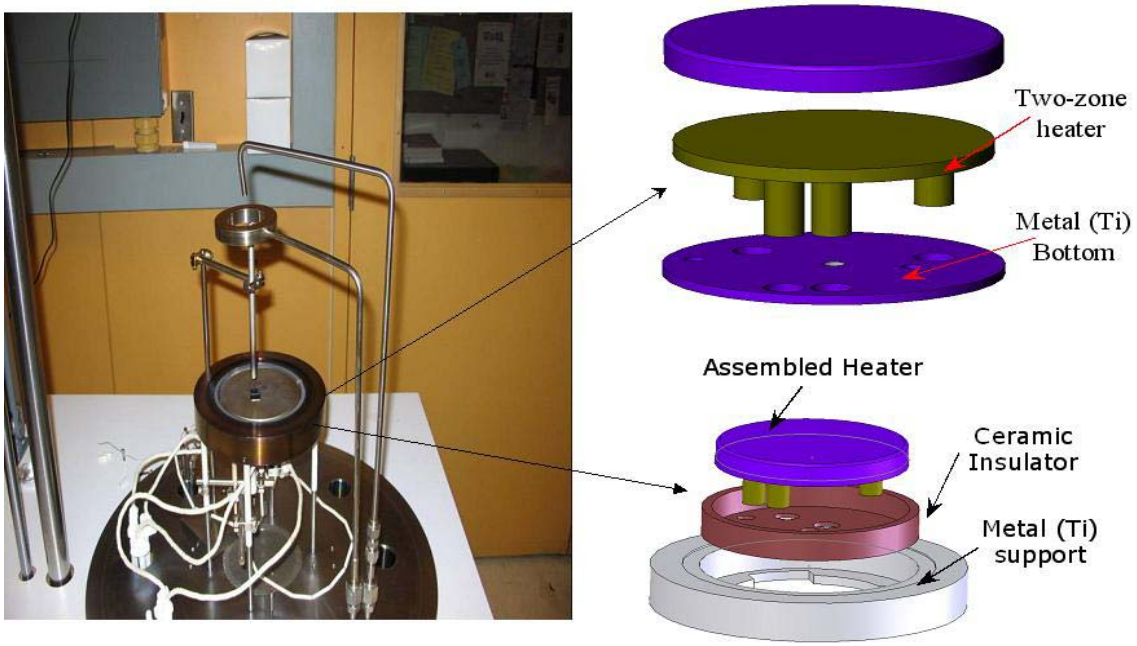


Figure 5-1: CNT machine chuck-1

5.2 Design analysis of CNT machine chuck-2

Figure 5-2 shows the second design of CNT machine chuck to overcome the limitation of chuck-1 design. Chuck-2 had a ceramic circular support and ceramic posts which holds the heater assembly. The reason for replacing the metal with ceramic is because; the chuck is electrically isolated and this results in uniform plasma. A better type of thermocouple was used, which had following feature: withstand temperatures up to 1090°C, high temperature ceramic insulation with Inconel over braid, flexible and abrasion resistant. In this design the cathode electrical connection is made from the side instead from the bottom as shown in

figure 5-2. The advantages of this chuck design were: the plasma was stable during the growth of CNTs, uniform temperature distribution and there were no sparks.

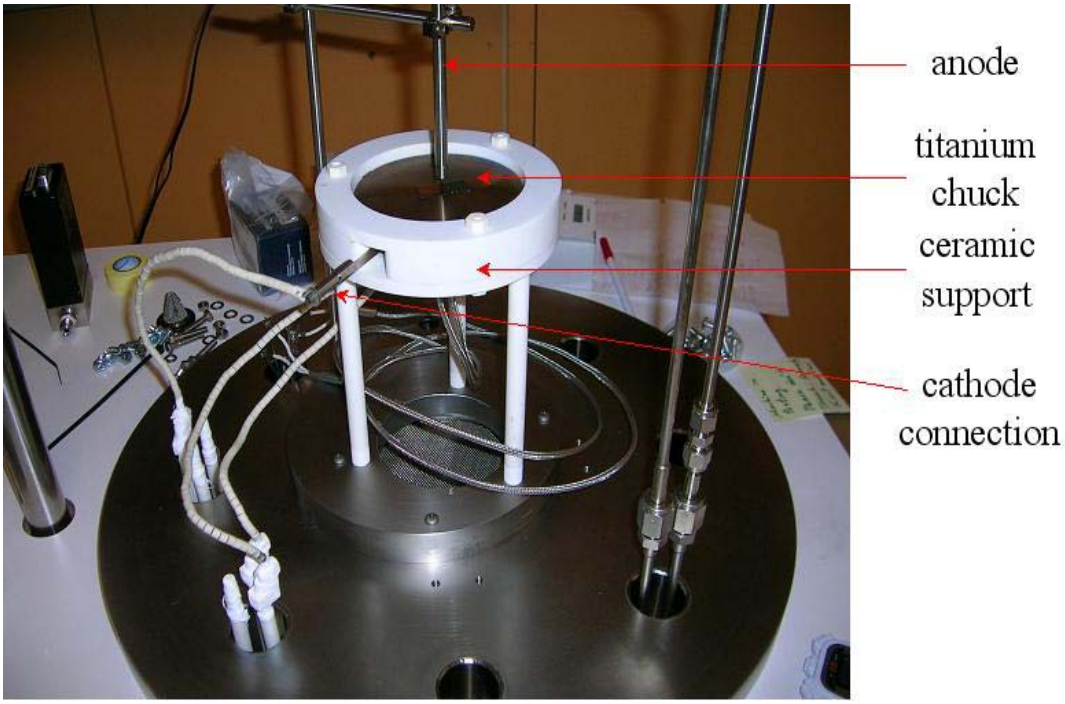


Figure 5-2: CNT machine chuck-2

After prolonged use of the chuck there were many problems like: ceramic support cracked due to mismatch in thermal expansion, carbon deposition on the top surface of chuck, machine took long time to cool down due to ceramic parts, inconsistent plasma after long use of the machine and had difficulty to assemble and disassemble parts. Hence, a new design of chuck (chuck-3) was made to overcome some these limitations.

5.3 Design analysis of CNT machine chuck-3

Figure 5-3 shows the third design of CNT machine chuck to overcome the limitation of chuck-2 design. Chuck-3 had a ceramic circular support and ceramic posts, which holds the heater assembly and 6 inch diameter base plate. This six-inch diameter titanium base plate blocks the deposition of carbon on ceramic parts. A 6-inch diameter anode was used to distribute the plasma consistently across a 6-inch wafer, though larger plasma power was needed to ignite. Six-inch diameter chuck was mainly made to accommodate 6-inch wafer, so that the post-processing can be done with the 6-inch machines at MIT. Six-inch diameter chuck failed to produce good CNTs because of the severe drop in temperature on the top surface of the cathode and the lower current density of the plasma over the substrate. The

details of failure analysis are discussed in the following chapters in terms of heat transfer and plasma density.

Figure 5-3: CNT machine chuck-3

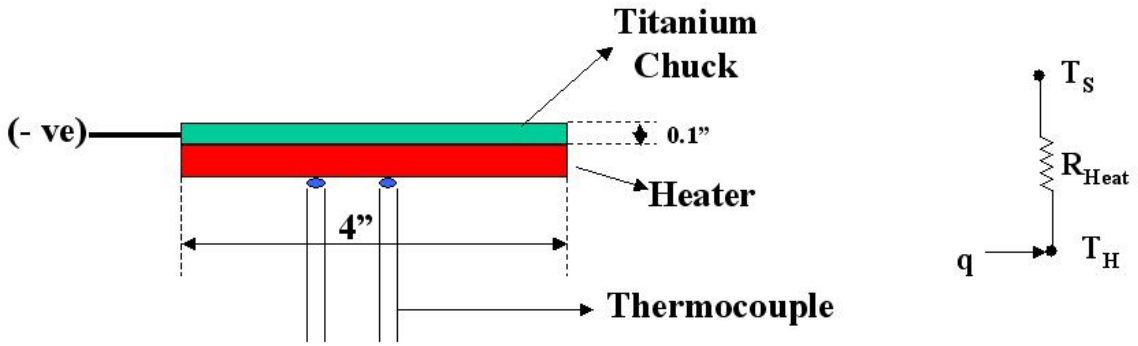
5.4 Failure analysis of CNT machine chuck-2 & 3

Both the designs (chuck-2 & 3) as shown in figure 5-2~3 has an outer ceramic holder mounted on the ceramic posts. This makes the chuck electrically floating preventing sparks and distributes the plasma uniformly over the surface of the wafer. A simple heat transfer model was proposed to find out the drop in temperature between top surface and heater surface and latter was checked experimentally using a thermocouple for both the designs. Plasma density calculations were also made for both the designs (chuck-2 & 3) using the following specification of plasma source: maximum power is 1KW, maximum voltage is 1KV and maximum current is 1A.

5.4.1 Heat transfer analysis of the 4-inch diameter chuck (chuck-2)

The 4-inch diameter chuck (chuck-2) has a heater with specifications: resistance of inner coil -18 ohm, maximum current - 13 A, thickness - 5mm, area of the heater = 78.5 cm^2 and flux needed to reach 650^{o}C is 14.5 W/cm^2. From these specifications it can be calculated that heat generated by the heater is around 1138Watts. Following assumptions are made in these

heat transfer model: convection and radiation heat transfer mode are neglected, heat produced due to plasma is not taken into considerations and 1-D heat conduction is only considered. A schematic representation and heat transfer model of 4-inch diameter chuck (figure 5-2) is shown in figure 5-4 (a-b).



(a) (b)

Figure 5-4: (a) Schematic representation of 4-inch diameter chuck (chuck-2) (b) heat transfer model

The 4-inch chuck (chuck-2) specifications are: thermal conductivity of Ti (k) –20.2 W/m-K, area of Ti chuck (A) –78.5 cm^2, chuck thickness (L)- 0.25cm, inner surface temperature (T_H)- 650°C (923°K) and outer surface temperature- T_s. The thermal resistance, heat generated by the heater and outer surface temperature are given by equations 5.1, 5.2 and 5.3 respectively.

Thermal resistance is given by, $R_{Heat} = \frac{L}{kA}$ (5-1)

Heat generated by the heater is given by, $q = \frac{(T_H - T_S)}{R_{Heat}}$ (5-2)

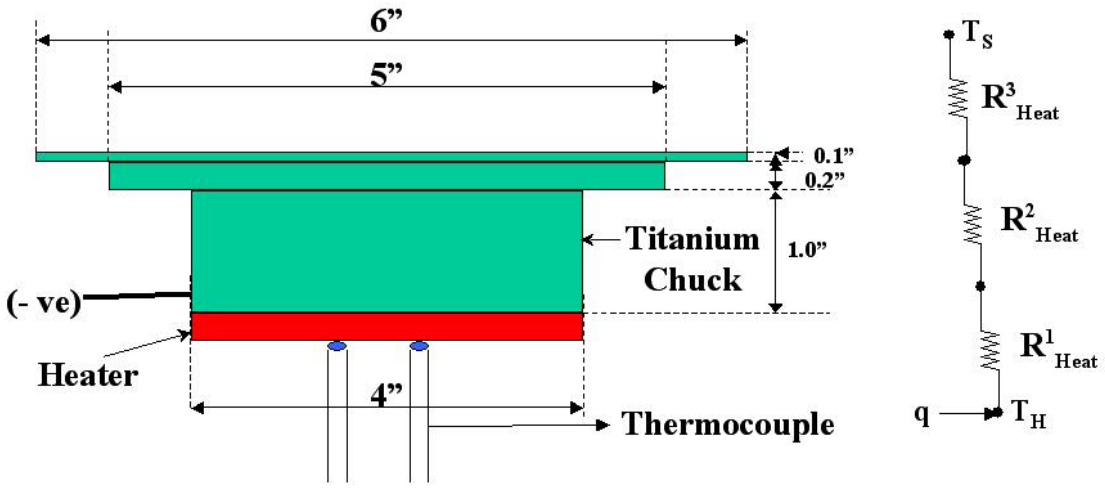
So outer surface temperature is given by, $T_S = T_H - q * R_{Heat}$ (5-3)

T_S=923-1138*$\left(\frac{0.0025}{20.2*0.00785}\right)$=905° K=632° C

A temperature difference of 18°C is obtained for a 4-inch chuck from the thermal model. This model was verified experimentally by mounting a thermocouple on the top surface of the titanium chuck. The heater of the CNT machine was maintained at a temperature of 650°C at vacuum and the mounted thermocouple showed a reading of 627°C indicating that there was a temperature difference of 23°C.

5.4.2 Heat transfer analysis of the 6-inch diameter chuck (chuck-3)

A schematic representation and heat transfer model of 6-inch diameter chuck (figure 5-3) is shown in figure 5-5 (a-b).



(a) (b)

Figure 5-5: (a) Schematic representation of 6-inch diameter chuck (chuck-3) (b) Heat transfer model

The 6-inch chuck specifications: thermal conductivity of Ti (k) –20.2 W/m-K, area of Ti chuck (A) –182.5 cm^2, inner surface temperature (T_H)- 650°C (923°K) and outer surface temperature- T_s. The thermal resistances, heat generated by the heater and outer surface temperature is given by equations 5.4, 5.5, 5.6, 5.7 and 5.8 respectively.

First thermal resistance is given by, $R^1_{Heat} = \frac{L_1}{kA_1} = \frac{0.025}{20.2*0.00785} = 0.15K/W$ (5-4)

Second thermal resistance is given by, $R^2_{Heat} = \frac{L_2}{kA_2} = \frac{0.005}{20.2*0.0127} = 0.019K/W$ (5-5)

Third thermal resistance is given by, $R^3_{Heat} = \frac{L_3}{kA_3} = \frac{0.00254}{20.2*0.0182} = 0.006K/W$ (5-6)

The heat generated by the heater is given by, $q = \frac{(T_H - T_S)}{\sum R_{Heat}}$ (5-7)

The outer surface temperature is given by, $T_S = T_H - q*\sum R_{Heat}$ (5-8)

$= 923 - 1138*0.17 = 729^o K = 456^o C$

A temperature difference of 194°C is obtained for a 6-inch chuck (chuck-3) from the thermal model. This model was verified experimentally by mounting a thermocouple on the top surface of the titanium chuck. The heater of the CNT machine was maintained at a temperature of 650°C at vacuum and the mounted thermocouple showed a reading of 417° C indicating that there was a temperature difference of 233°C. There is mismatch between theoretical thermal model and experimental values because in the model the effect of convection and radiation heat transfer mode are neglected.

5.4.3 Plasma calculations of 4-inch and 6-inch chuck (chuck-2 & 3)

For a 4-inch diameter chuck (chuck-2) the process required to obtain nice vertical CNTs are: temperature of 550-600°C, plasma power of 250-300W and plasma voltage of 500-510V. So the plasma current required is 0.5-0.6A and the area of 4-inch chuck is 0.00811m^2. From these values the current density is around 61-74 A/m^2. For a 6-inch diameter chuck (chuck-3) the process required to obtain nice vertical CNTs are: temperature of 580-600°C, plasma power of 450-500W and plasma voltage of 500V. So the plasma current required is 0.9-1.0A and the area of 6-inch chuck is 0.01824m^2. From these values the current density is around 49-54 A/m^2. Hence the current density for 6-inch chuck (chuck-3) is less compared to 4-inch chuck (chuck-2). To obtain an average current density of 67.5 A/m^2 as calculated from 4 inch chuck, we need a current of 1.2 A by the 6 inch chuck, but the plasma source can pass a maximum current of 1 Amperes. So it would be impossible to reach higher current density with 6-inch chuck.

From the heat transfer analysis and plasma calculations following conclusions were obtained: a temperature drop of around 200°C was obtained by the 6 inch chuck and current density drops by 16A/m^2 (76%) when 6 inch chuck is used. Hence 6-inch chuck (chuck-3) design was a failure.

5.5 Robust CNT chuck design

Design of CNT chuck is important for the growth of longer and vertical single stranded CNTs. Earlier designs of CNT chuck as shown in figure 5-1~3 produced single stranded CNTs which were smaller in length, bent and had amorphous carbon. These earlier designs of CNT chucks had also following draw backs: ceramic chuck cracked due to heat, carbon

residue on metal parts, showed inconsistent plasma after longer use of the machine, machine takes long time to cool down, lots of metal and ceramic parts, difficult to assemble and disassemble parts and non-uniform temperature distribution. A new design was made to over these limitations. The new robust CNT chuck design is shown in figure 5-6. It has four main parts: wafer holder, heater holder, ceramic pillars and thermocouple holders.

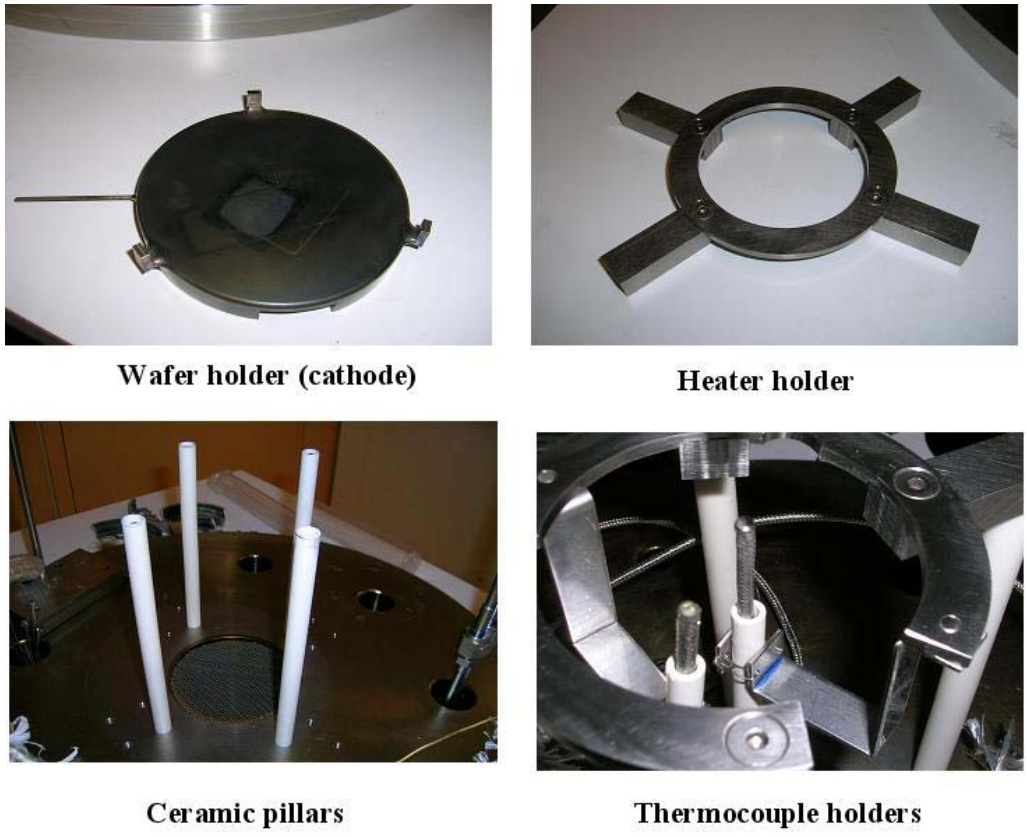


Figure 5-6: Parts of robust CNT chuck

Assembly of all the parts is as shown in figure 5-7. This design has following advantages as compared to earlier designs: Assembly of all the parts is fast, no sparks and plasma is very stable, wafer holder can be easily detached and cleaned, no problem of ceramic cracking, the whole run time of the machine is very less, heater sits on thermocouples (temperature measured is accurate) and 4-inch wafer holder is used so there is higher current density.

Figure 5-7: Assembled robust CNT chuck

CHAPTER 6

SINGLE STRANDED CNT GROWTH

The additive process flow for single stranded CNT as discussed in section 2.2.2 requires placing of nickel nano-dots in deterministic location and growing of carbon nanotubes using optimized process condition. This chapter discusses about making nickel nano-dots, placing them in deterministic location (using scanning electron beam lithography), issues in making these nano-dots, finding optimized process conditions for growing of single stranded CNTs and comparison of shape of nano-dots with single stranded CNTs.

6.1 Making of nickel nano-dots

According to most of the literature nickel nano-dots arrays are made by using a highly sensitive bi-layer resist composed of low and high molecular weight PolyMethyl MethAcrylate (PMMA)[9]. Usually 5% 100K MW (molecular weight) PMMA or Polymethylglutarimide (PMGI) is used as a lower layer and 2% 950K MW PMMA is used as upper layer to obtain precise undercut control during liftoff process. In this thesis a new process (single layer of PMMA) for making nickel nano-dots is proposed instead of using conventional bi-layer of PMMA. This process is cost effective because use of expense chemicals like 100K MW PMMA, PMGI or CD26 developer is avoided and also it takes less time to make nickel nano-dots.

6.1.1 Titanium Deposition

1) Turn on cooling waters to the hearth and power supply of e-beam metal evaporator and vent the chamber to atmospheric pressure.

2) Load a p-type <100> 4-inch silicon wafer into the evaporator and make sure that the clip spring is positioned in such a way that it points directly toward the center of the wafer. Open the shutter and place the crucible with the deposition material (titanium) into the hearth pocket.

3) Close the chamber and pump the system to reach a pressure of $2*10^{-6}$ or lower before depositing metal.

4) After high vacuum is reached the crucible with metal is heated by e-beam till it starts evaporating. A deposition rate of $2A^0$/sec is used for depositing 25 nm thick metal.

5) Turn off the filament and the high voltage at the power supply controller and wait for some time so that the chamber cools down.

6) Vent the chamber till it reached atmospheric pressure and unload the wafers.

6.1.2 PMMA Mixing

PolyMethyl MethAcrylate (PMMA) is a positive photo resist, which is used to produce high contrast, high-resolution features using e-beam. Standard PMMA products include 495,000 and 950,000 molecular weights (MW) in a wide range of film thicknesses formulated in chlorobenzene. The procured PMMA from the vendor is 6% 950KPMMA in chlorobenzene, which produces thicker resist hence it has to be diluted. The thickness of the PMMA depends on the dilution of the PMMA in cholorobenzene, spin-speed and duration of spin. The desired thickness of PMMA required for exposure is 75-100nm, so the PMMA has to be diluted to 1.5% 950KPMMA in cholorobenzene. Dilution is done as follows:

1) RCA cleaned container, measuring cylinder, bottle and stirring rod procured from lab supply.

2) Mix base PMMA and cholorbenzene by volume to achieve desired dilution of PMMA (1.5% in cholorobenzene) using dedicated graduated cylinders.

3) Mix the two chemicals using stirring rod for 5-10 minutes and store it in a bottle with a tight cap.

4) Clean container, measuring cylinder and stirring rod after use with acetone, then IPA, then flushing with DI water.

6.1.3 PMMA Coating

1) Set spinner to desired speeds: spread speed- 500rpm for 5seconds and spin speed-3500rpm for 30 seconds.

2) Center the wafer containing 25nm thick titanium on the spinner chuck and turn the vacuum ON.

3) Using pipette, measure out a few mL's of PMMA mix from bottle and spread it on wafer starting from the center to cover half the wafer area.

4) Ensure spin speed/timer properly set, start spinner and let run to desired time.

5) Switch the vacuum off on the spinner.

6) Place wafer on vacuum hotplate set to 180°C for 90 seconds, so that PMMA hardens and then store wafers in 4" individual carrier.

6.1.4 Exposure using scanning electron beam lithography

Scanning electron beam lithography system used for exposure is called Raith-150. The Raith 150 is an SEM modified for e-beam lithography and has a maximum operating voltage of 30Kev. It has an acceleration voltage variable from 1-30kV and an approximate beam diameter (for low currents) of 3 nm. The pattern generator can deflect the beam at effective speeds of about 1 MHz and can write field sizes between 50 and 300 microns. The step size on this tool is fixed at 2nm. This tool has written isolated lines as fine as 17 nm and gratings with a pitch of <70 nm.

1) The make the design or pattern (dots of different sizes and doses) using Raith-150 software, structure the design using different layers or hierarchy and the transfer design to lithography computer.

2) Wafer containing 75-100nm thick PMMA is mounted on Raith-150 chuck with spring loaded clamps.

3) Put three gold dot solutions on the centre of the wafer in triangular fashion and wait till it dries. The reason for using gold dots is because it is used for adjusting SEM parameters like focus, aperture alignment and stigmation.

4) Load the wafer into the Raith-150 machine and switch the vacuum pump ON. Reset the co-ordinate system, switch the beam ON, use the acceleration voltage of 10 KeV and aperture size of 20 um.

5) Level the stage of Raith-150 machine by using the PZTs. Focus on the gold dots and zoom in, adjust the stage level again by using the PZTs.

6) Adjust focus, aperture alignment and stigmation of the SEM by focusing on the gold dots.

7) A manual field calibration is done using different scan sizes, resolution of 512 and different placements.

8) Measure the current by using a Faraday's cup, which is present on the chuck.

9) Note the X, Y co-ordinates of the positions where exposure is done and reset the U, V, W co-ordinate to zero.

10) Set the exposure parameters: area step size of $0.04\mu m$, area of dose of $60\mu As/cm^2$ and area dwell time more than 0.0001 milliseconds.

11) Open the pattern file (GDSII format) and start exposing the wafer using electron beam.

12) Unload the wafer after exposure from SEM and store it in a wafer carrier box.

6.1.5 Developing PMMA

1) Obtain MIBK (methyl-iso-butyl-ketone) and iso-propanol from pass-through.

2) Under hood, mix 2:1 IPA and MIBK in glass container for 5-10 minutes; monitor temperature until 21ºC is reached.

3) Develop wafer in the glass container for 90 seconds and then rinse wafer with iso-propanol for 30 seconds.

4) Return all chemicals to pass-through; rinse glassware and thermometer and return to racks.

6.1.6 Deposition of Nickel

Same process step are followed as discussed in section 6.1.1 to deposit nickel. 15 nm of nickel is deposited over PMMA developed wafers.

6.1.7 Liftoff of nickel

1) This steps requires the heating of NMP (1-methyl-2-pyrrolidinone) to 90ºC (flash point 93ºC, auto-ignition >300ºC) and must be done in a fume hood.

2) Prepare hotplate, a large glass container for an outer bath, and a smaller glass container as the inner bath (this prevents the inner bath from heating past 100ºC).

3) Fill the outer container with DI water, and the inner container with enough NMP to cover the wafer

4) Set and start the hotplate for 90ºC, await inner bath temperature to reach this point.

5) Dip the wafers or wafer pieces with Teflon holders, monitor the liftoff. To remove larger pieces of PMMA/nickel pull the wafer out, rinse the wafer with acetone; without allowing the acetone to dry and return the wafer to the NMP bath.

6) When the liftoff is complete remove the wafer and rinse with IPA for 30 seconds, turn off the hotplate and allow the bath to cool before disposing in the solvent drain. Rinse and return all glassware and thermometer to rack.

The new process flow of making nickel nano-dots involving deposition of titanium, spin of PMMA, exposure of PMMA, deposition of nickel and liftoff is shown in Figure 6-1. The result obtained from this new process is shown in figure 6-2, where the all dots are circular is shape and 250-300nm diameters in size. Hence this new process (single layer PMMA) is economical compared to using bi-layer of PMMA. An AFM scan was done on the nickel nano-dot as shown in figure 6-2 to observe the surface topography and measure the actual thickness of nickel after liftoff, which is shown in figure 6-3. From the AFM scan it is observed that the thickness of nickel dot is 17nm and the top surface is quite smooth.

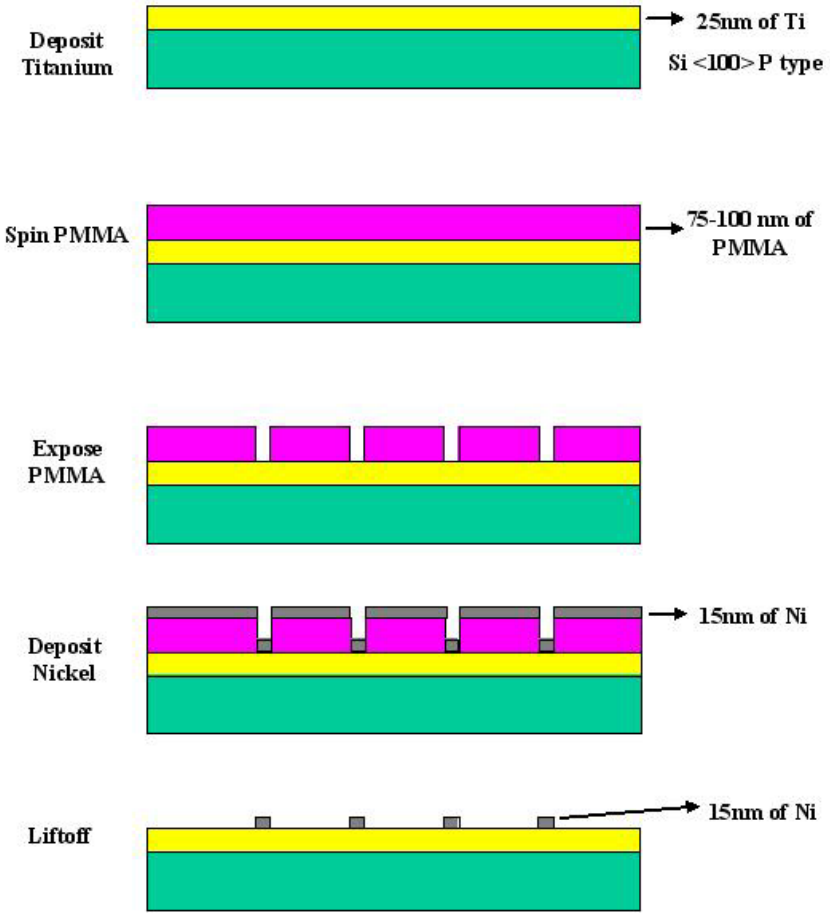


Figure 6-1: The process flow of making nickel nano-dots

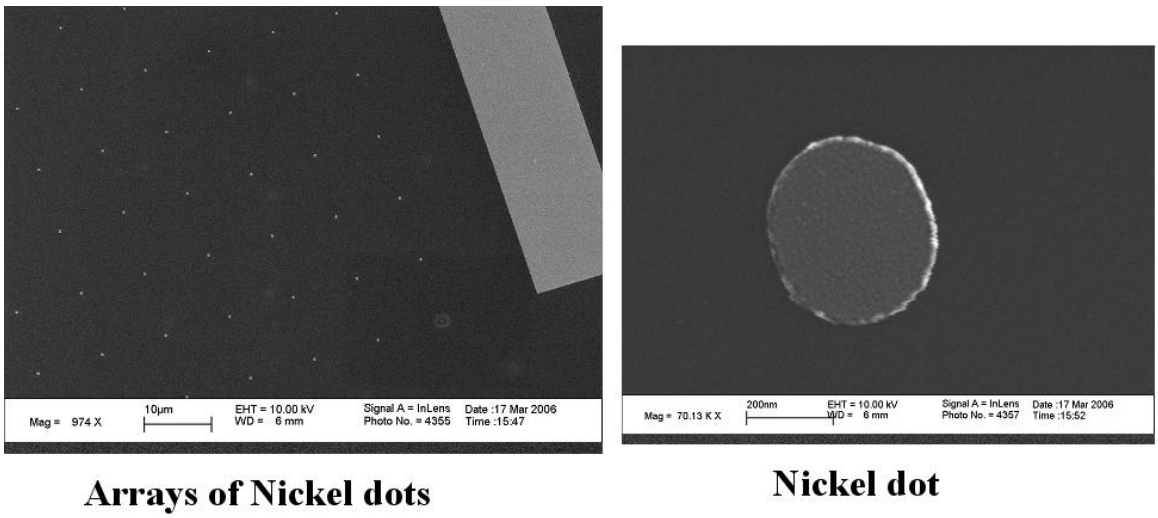


Figure 6-2: Arrays of nickel nano-dots

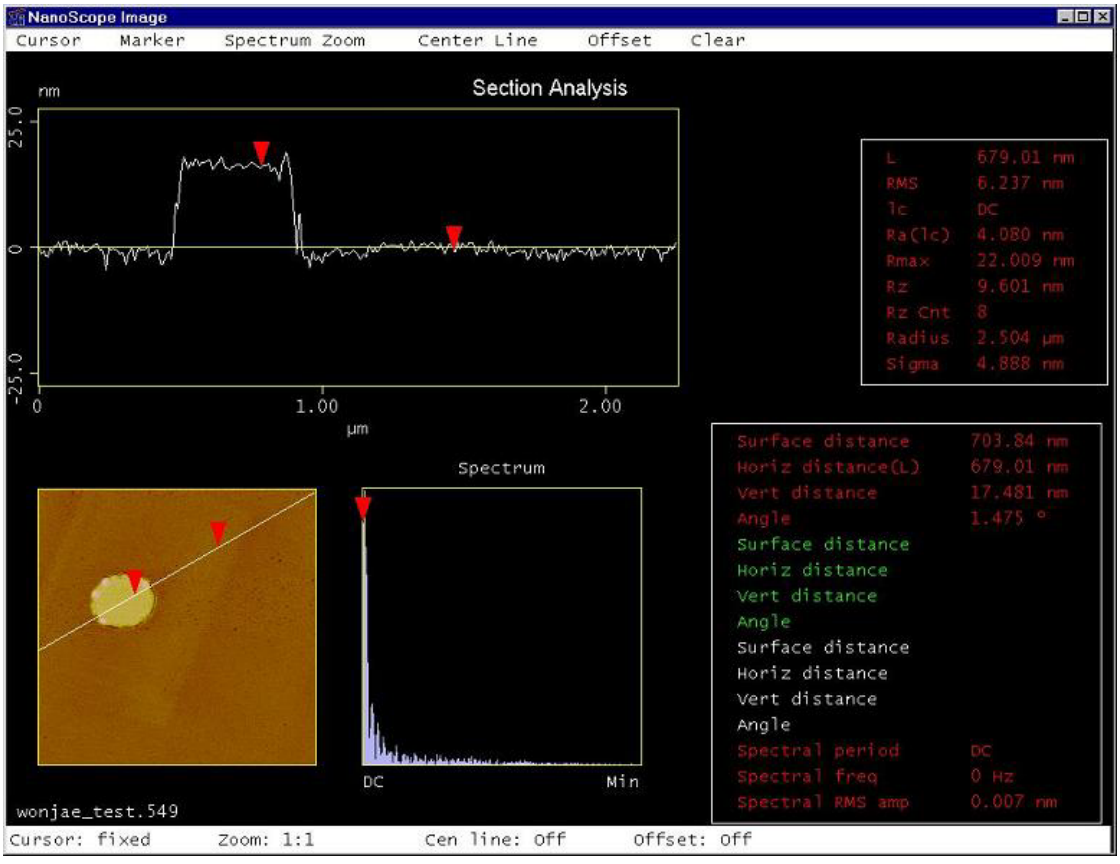


Figure 6-3: AFM scan of nickel nano-dot

6.1.8 Single stranded CNT growth

The new CNT chuck configuration (figure 5-7) was used to grow single stranded CNTs. The samples used had titanium layer of 25 nm thickness and nickel nano-dots are 15nm thick and 100-250nm size as shown in figure 6-2 is loaded into carbon nanotube machine. The process conditions of carbon nanotube machine used are: distance between anode and cathode 0.55 inches, temperature growth 580^{O} C (ramp up rate 20^{O} C per minute), 160 sccm of ammonia passed for 7 minutes, pressure maintained at 8 Torrs, plasma voltage: 530 volts (voltage controlled mode), plasma power: 430 – 230W, and CNT growth time is 14 minutes. The single stranded CNTs grown 5um and 10um apart are shown in figure 6-4. These CNTs are 10um long and have conical in shape. The CNTs grown are longer (5-10um) because: nickel nano-dots where quite circular in shape (as shown in figure 6-2), plasma was very stable and uniform throughout the run and temperature was uniform across the wafer.

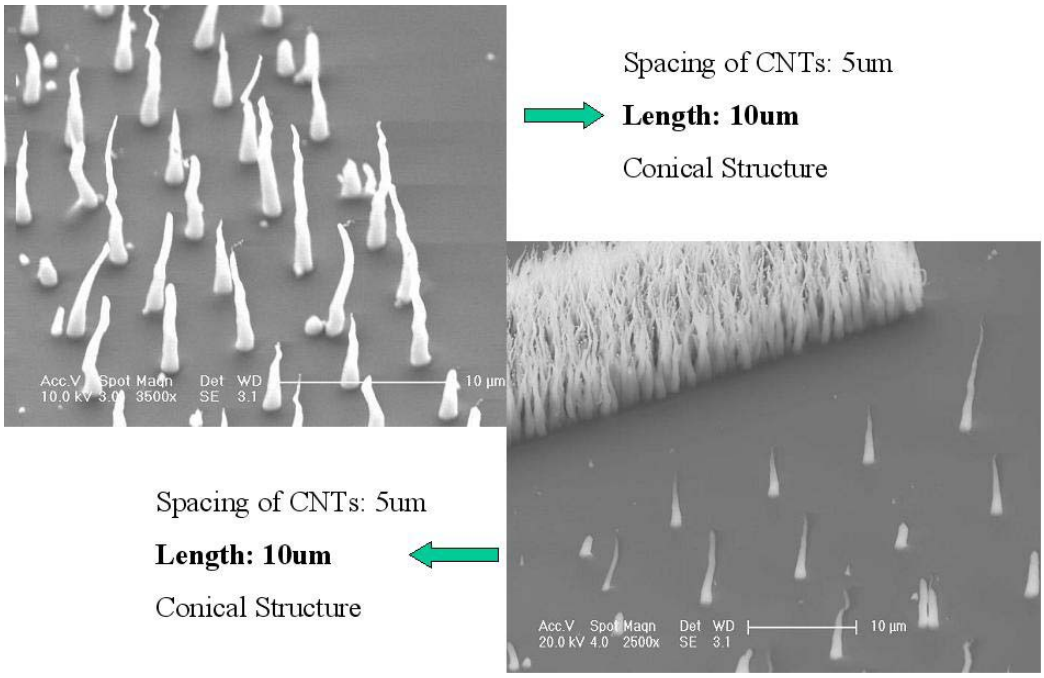


Figure 6-4: Single Stranded CNTs grown 5um and 10um apart

6.2 Issues in making of nickel nano-dots

The process plan discussed in section 6.1, had a layer of titanium below PMMA resist. A different process plan was followed where titanium and nickel was deposited after PMMA was exposed in order to reduce the number of steps (avoid e-beam deposition twice). The

process plan is shown in figure in 6-5. A 1.5% 950K PMMA in cholorobenzene was spin coated on a 4-inch silicon wafer. Scanning electron beam lithography (Raith-150) machine was used to expose the resist so that circles with 100-250nm diameters were formed using the same parameters discussed in section 6.1.4. After exposing the wafer was developed in 1:2 IMBK: IAP solutions for 90 seconds. A 25nm of Ti and 15nm of Ni was deposited. Lift-off was done using NMP chemical in a hot water bath as discussed in section 6.1.7.

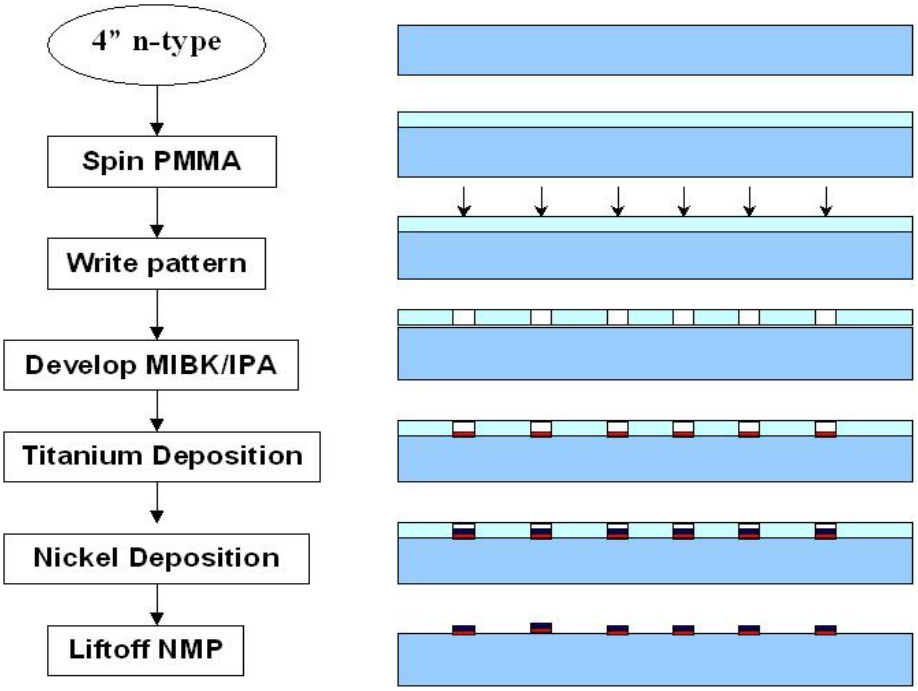


Figure 6-5: Process flow for making nickle nano-dot

Figure 6-6 shows SEM pictures of nickel on top titanium nano-dot formed after NMP lift-off. The edges of these dots are rough and the top surface is not flat but warped as represented in figure 6-6. This may be because there was no undercut when PMMA was exposed and so single layer of PMMA is not suitable to make a flat bi-layer of metal nano-dot. Carbon nanotubes are not grown properly but there was deposition of carbon on these dots as shown in figure 6-7. There was no tip growth of carbon nanotubes because nickel was not separated from the titanium patch and carbon deposited on the surface of nickel instead. For a tip growth of carbon nanotube, the separation of the interface between Ni and Ti is important. When there is a strong adhesion between Ni and Ti, there may be no deposition of carbon between the two metal patches and there is no growth of carbon

nanotube as a result. The dome shape of the dots might have made the adhesion between Ni and Ti stronger which lead to no growth of CNTs.

The main conclusions from the above sections (6.1, 6.2) are: 1) To obtain nice vertical single stranded CNTs we need to deposit single layer of metal (nickel) on a single layer of PMMA 2) Bi-layer metal deposition on single layer of PMMA leads to no growth of CNTS. 3) If bi-layer of metal deposition has to be done we need to use bi-layer of PMMA composed of low and high molecular weight or PMGI with PMMA.

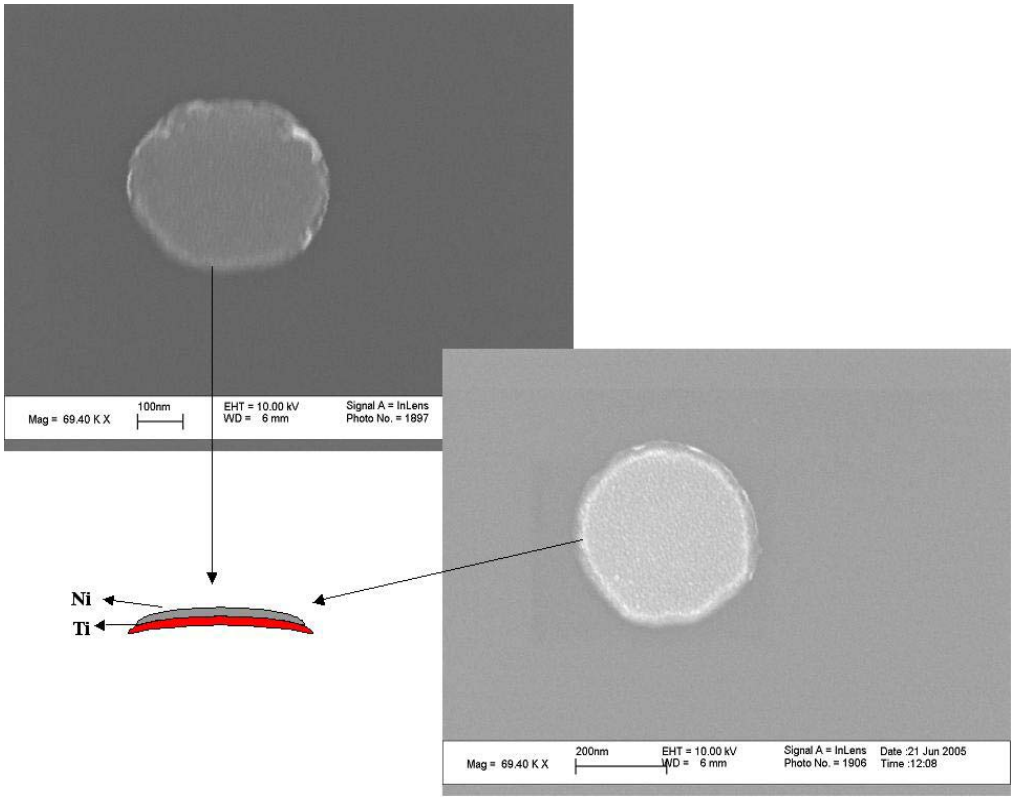


Figure 6-6: SEM picture of nickel and titanium nano-dot

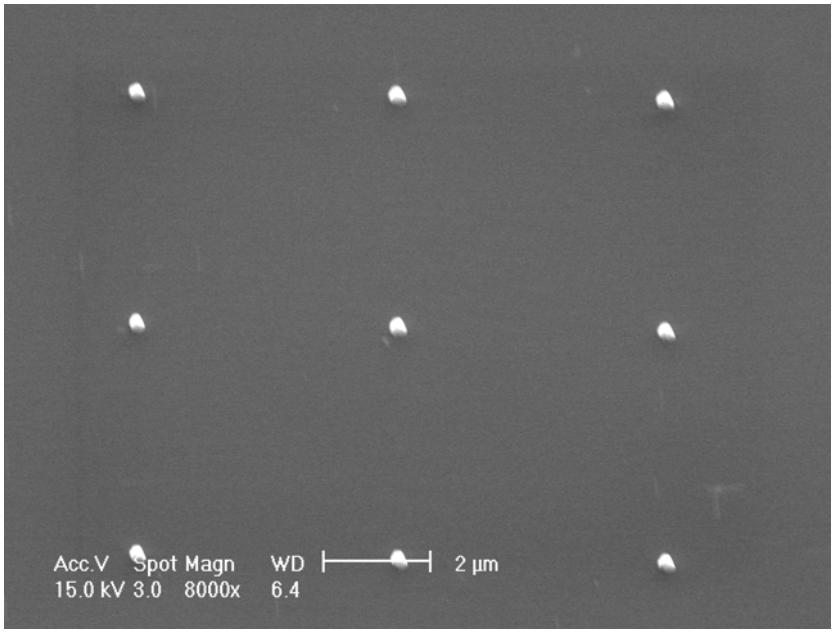


Figure 6-7: Carbon deposition on nickel nano-dot

6.3 Comparison of Nano Dot shape with Single Stranded CNTs

A comparison study was made to understand the effect of shape of nickel nano dots on single stranded CNT growth. These nickel nano dots are made as described in section 6.1, which results in circular or non-circular shapes. Non-circular dots are produced because of the following reasons: no undercut during PMMA exposure, thicker PMMA resist, lower current dose, small exposure time, irregularities during developing the PMMA resist and abnormality during the metal lift-off. An irregular shaped nickel nano dot produces a bent CNT with amorphous carbon around it as shown in figure 6-8. If the nickel nano dot is irregular and bigger, two or three carbon nanotubes are grown at the same spot. A circular nano dot of size 200nm or 250nm produces nice vertical single stranded CNT as shown in figure 6-9. So this study shows the importance of shape of nickel nano dot to produce good cylindrical single stranded CNT.

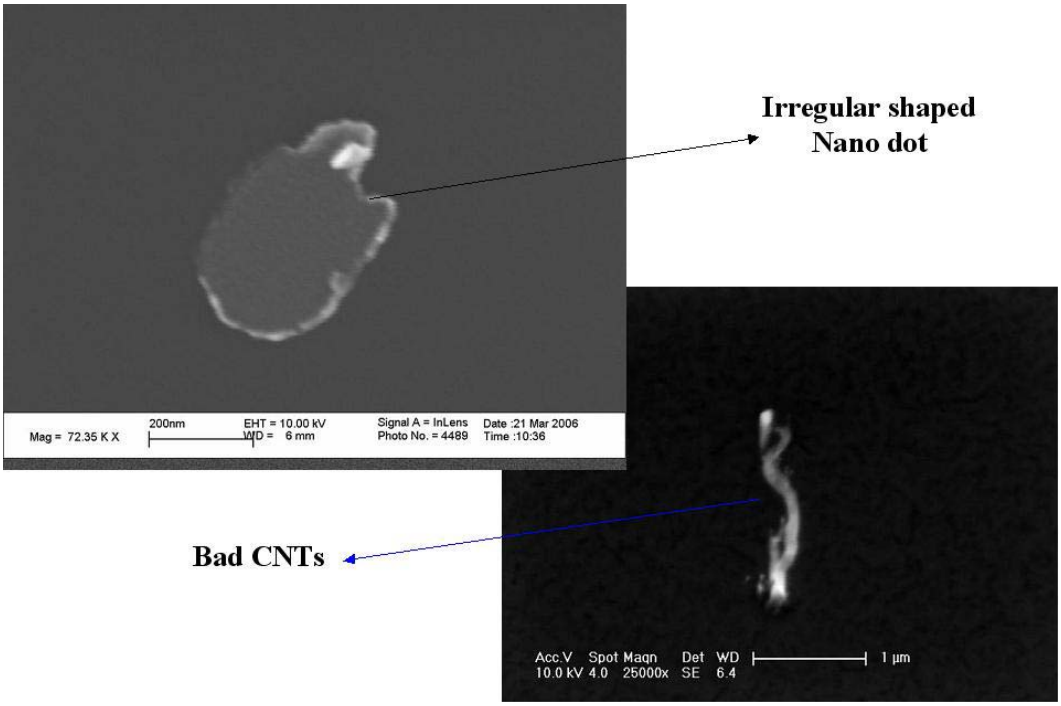


Figure 6-8: Irregular shaped nickel dot produces non vertical CNT

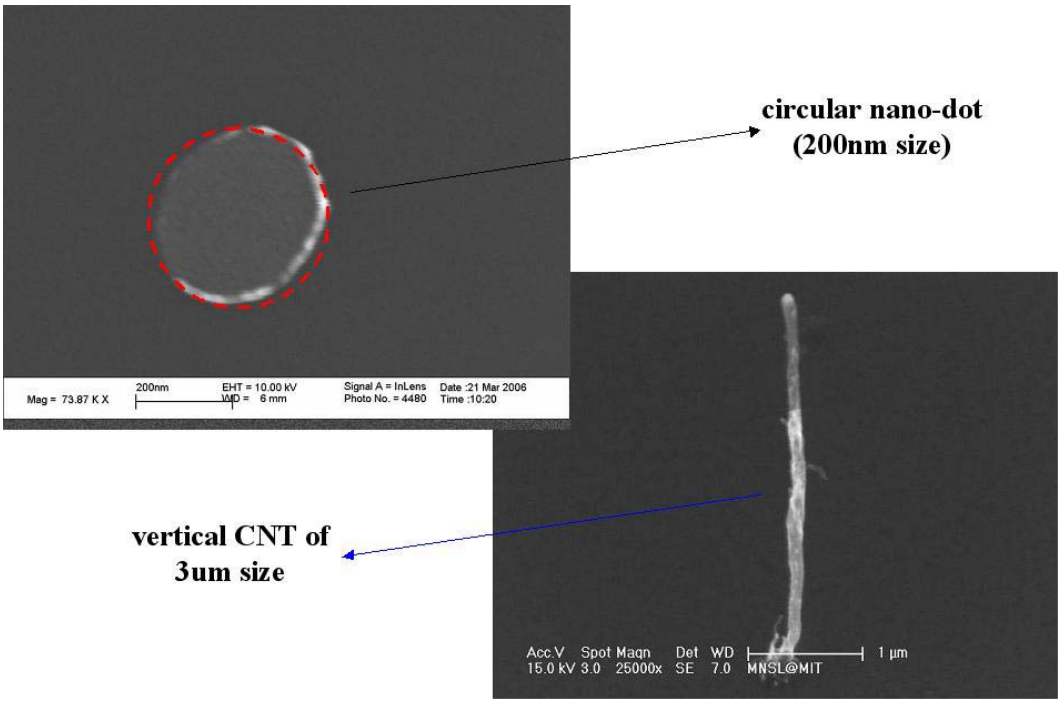


Figure 6-9: Circular nickel dot produces vertical CNT

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

This thesis discusses the design and analysis of a PECVD system to grow uniform, vertical, long single stranded carbon nanotubes and address the issues that exist due to variation in design, plasma inconsistency and irregularity of temperature. A new design of PECVD system is proposed and it has a very stable plasma and uniform temperature across the wafer holder. A new recipe to make nano-dots is presented, which acts a template to grow single stranded carbon nanotubes and grow vertical CNTs at deterministic location. These nickel nano-dots were placed in exact locations and were quite circular in shape. Process conditions and machine parameters to obtain efficient results were successfully obtained for scanning electron beam machine, e-beam deposition and PECVD system. Using optimized process conditions 10um long single stranded CNTs was grown. A brief summary of research work presented in this thesis is shown in figure 7-1.

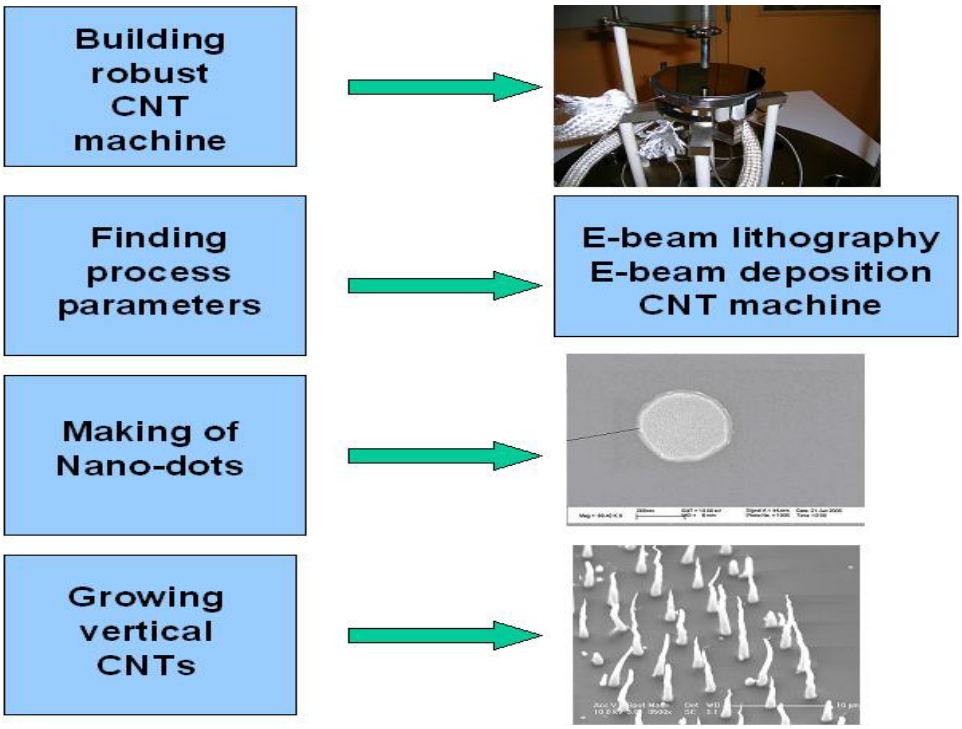


Figure 7-1: Summary of research presented in this thesis

7.2 Future Work

The future work would be to characterize the CNTs using TEM and to make polymer pellets with embedded single stranded CNTs of specified geometry. Then these pellets with exposed CNTs are transplanted to specific locations, where it can be used as In-plane AFM probe for scanning a surface or integrated with a device for micro-fluidic, photonic and electronic transfer. This opens up an opportunity of using this method to harvest nanopellets and reassemble them in large scale onto acceptor substrate, creating CNT-based devices that could not otherwise be reliably made. The future work to be done is represented in figure 7-2.

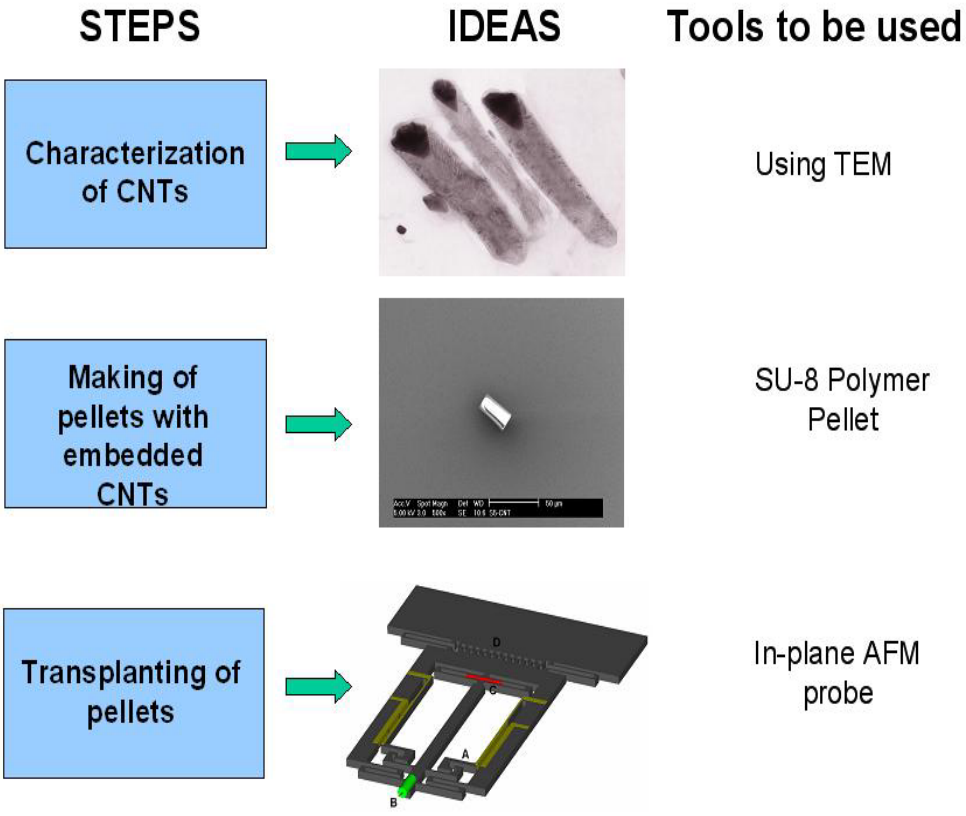


Figure 7-2: Future work

The in-plane AFM probe design as shown in figure 7-2 features a switchable stiffness, which adopts itself to the changing surface hardness of the sample [5]. The variable stiffness is accomplished in a mechanical way by engaging or disengaging auxiliary beams to the compliant beam structure by means of electrostatically actuated clutches. The vertical displacement of the tip can be measured by a capacitive sensor, which can easily be

integrated into the system. It is designed to have a single strand multi-walled carbon nanotube tip assembled at the end of the beam, a built-in actuator and a tip deflection sensor, all in the same plane. The coplanar design facilitates the assembly of a carbon natotube (CNT) tip to the MEMS structure and the fabrication of massively parallel arrayed tips.

For an energy flow through the nanocandle, a hollow nanocandle will be filled with a metal core (shown in Figure 7-3) to conduct thermal energy to the CNT tip. One possible way to accomplish the photonic/thermal energy conversion is to use an optical fiber connected to the candle and keep the photothermal energy confined inside the core as shown in figure 7-3. A design may involve a nanocandle assembled into a V-grooved silicon substrate and aligned with the core of an optical fiber. Once placed in the groove, the nanocandle and an optical fiber can be fixed with a drop of epoxy. This manual assembly technology will be used for the transduction of very small quantities of photonic and electric energy. Multiple parallel assemblies of CNT tips can be done by fluidic self-assembly of nanocandles if a massive array of CNT tips is needed.

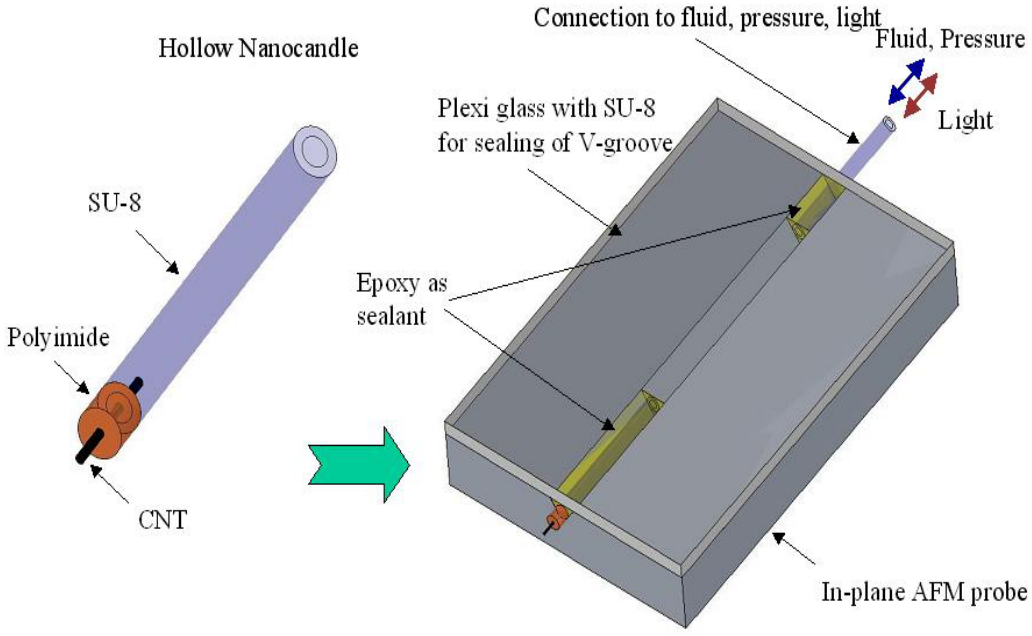


Figure 7-3: Hollow Nanocandle for Transport of Fluid and Photonic Energy

In order to improve Raman spectroscopy, a metal-coated AFM tip or a STM tip can be brought into contact with a sample surface. A schematic of the in-plane system for TERS

is shown in figure 7-4. A metal coated Carbon Nanotube (CNT) with a small diameter tip and high aspect ratio is ideal for this. This tip-enhance Raman spectroscopy (TERS) provides highly localized enhancements and offers a more uniform enhancement when scanning over the molecular scale sample. Optical resonance at the metal tip is essential, and a tip with a smooth surface, a sharp end, and small tip radius is ideal for the tip-enhanced Raman processes. Ag, Au, and Cu are the materials currently used as metal tips in TERS. It is expected that the CNTs' plasmonic behavior and the variable stiffness of the in-plane probe can further enhance Raman signals, thereby providing a high enough sensitivity for the imaging of single molecular structures, such as proteins.

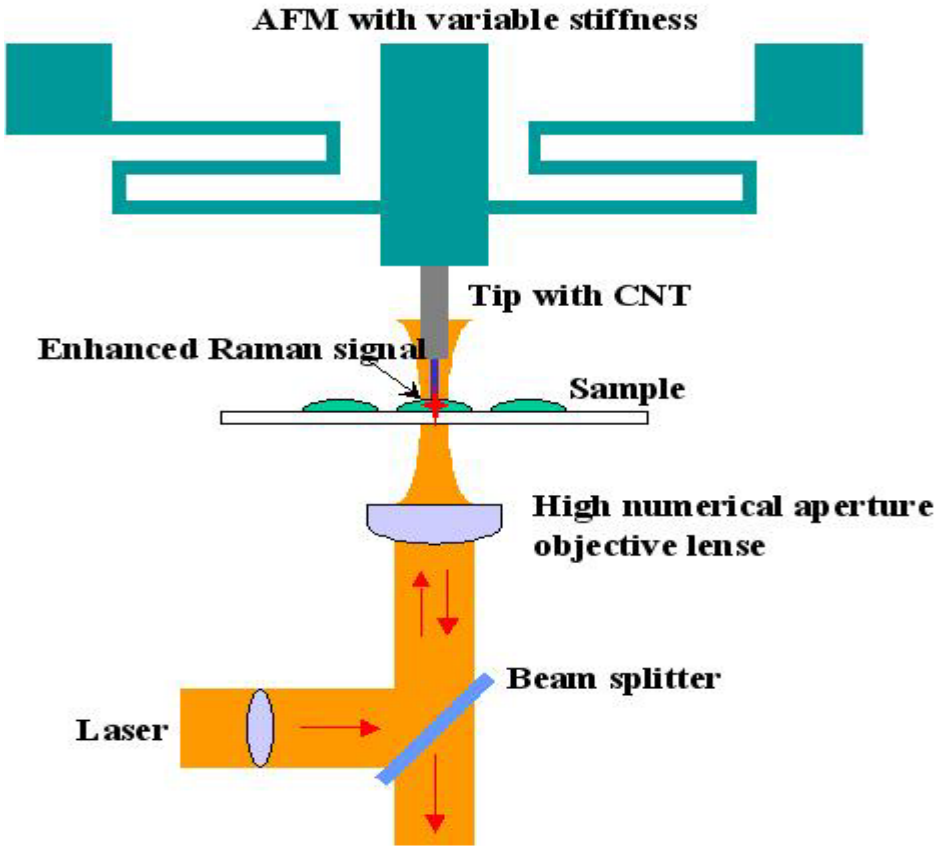


Figure 7-4: Schematic view of CNT tip used for Tip enhanced Raman spectroscopy

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