Master's Thesis
석사 학위논문

The Study of Nano-optical Antenna Array Structure for Nano-device

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Advisor : Professor Jae Eun Jang

Co-advisor : Professor Hongsoo Choi

By

Jaehan Im

Department of information and communication engineering

DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of [Master of Science in the Department of information and communication engineering. The study was conducted in accordance with Code of Research Ethics[1]

12. 03. 2012

Approved by

Professor 장 재 은 (Signature)
(Advisor)

Professor 최 홍 수 (Signature)
(Co-Advisor)

[1] Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

The Study of Nano-optical Antenna Array Structure for Nano-device

Jaehan Im

Accepted in partial fulfillment of the requirements for the degree of Master of Science.

12. 03. 2012

Head of Committee Jaeeun Jang (인)

Prof. 장 재은

Committee Member Hongsoo Choi (인)

Prof. 최 홍수

Committee Member Jiwoong Choi (인)

Prof. 최 지웅

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ABSTRACT

Nano antenna, coupling between terahertz level electro-magnetic wave and electrical signal, has been researched as an interest topic for terahertz communication and optoelectronics. In traditional antenna theory, the antenna length has strong relationship with wavelength. Especially, the formula that is a function of antenna size, wavelength, light velocity and frequency can be partly applied to terahertz communication. Therefore, multi-antenna structure with different length from micrometer to nanometer can have various resonant frequencies in ultra-high frequency region. However, the high resistance of metal nanostructure and the complicated fabrication process using 'Top-down' approach induce severe problems to the application in THz area.

The purpose of this work is to grow Carbon nanotubes (CNTs) which have different lengths at specific points. To grow single multi-walled CNT (MWCNT) on selected position, the patterned Ni catalyst and plasma enhanced chemical vapor deposition (PECVD) growth process were used. We investigated various CNT length formations with the control of catalyst size, acetylene ratio and temperature. For the experiment of catalyst size control, single CNT has grown on the catalyst which size is below 300nm. Although low temperature growth appears lower growth rate, it shows higher yield ratio of single CNT growth. CNT length is proportional to catalyst size. CNT thickness and length are longer and thicker with increasing C_2H_2 gas ratio respectively. From optimized process conditions, we get single MWCNTs with various heights on selected points using one step CVD process. The expected resonance frequency is from 50 to 130 THz as monopole antenna concept

Keywords: Nano-antenna, optical antenna, Nano structure, CNT growth

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Ⅰ. Introduction

1.1 Background

Recently, the driving frequency of electronic device is drastically increased due to high performance requirement and new applications. Traditionally, in communication area, the driving frequency has changed gradually from KHz to GHz level to store more information to electro-magnetic wave. The level is approached near THz range. In traditional antenna theory, the antenna length has strong relationship with wavelength. Especially, the formula that is a function of wavelength, light velocity and frequency can be partly applied to terahertz communication. When we roughly calculate the wavelength of antenna for coupling with terahertz, the length of antenna is about submicron to a few nano meters. As a communication device, Nano-antenna has been researched between the optics and the electromagnetic approaches. Recently, it is necessary to know that which approach is proper to terahertz communication.

One of new important applications using nano antenna is micro or nano size robot. Nano robot is a concept where it can kill a cancer cell in a body. In order to make nano-robot, wireless communication or power transmittance can be an essential function for its various working performance. Owing to the essential function of nano robot is an exchange of information, nano-antenna will be a part of nano robot due to a lack of surface area. In addition, due to size limit of device, the antenna structure can be assigned small dimension for making nano-size robot. For energy harvesting field, it can be expected to make better performance from advantages of wave nature instead of quantum nature in conventional photovoltaic cells. It can overcome limit of the band gap as well as a mount of lost energy as heat, which led to low efficiency below 50 %. Moreover, the higher efficiency is overtaken now with applying nano antenna concept using various height array structures due to the wideband absorption of

light spectrum. Therefore, multi-antenna structure with different length from micrometer to nanometer can have various resonant frequencies in ultra-high frequency region. Fig. 1.1.2 shows the concept of our multi-antenna with nano size. The antenna gets some information from light or tera hertz signal and couple it to the electrical signal. Each antenna plays a role to absorb different frequencies and emerge the signal the end of circuit. Nano-antenna can use not only terahertz communication but also solar cell due to the tera hertz frequency regime is overlapped light. Nano range matter, the study of nanotechnology is needed. [19]

Nanotechnology is understanding and control of matter at dimensions of roughly from 100nm to 1nm. This scale size and structure have directly related with properties and phenomena. Carbon nanotubes (CNT) have been researched a lot of electrical device due to their electronic and extraordinary mechanical properties such as ballistic electron transport and large elastic modulus. Carbon nanotube not only has electronic property, good current flow like Copper, but also appears the strength similar to diamond with high aspect ratio. These are the reason why we choose CNT as a best material to make a nano-antenna.

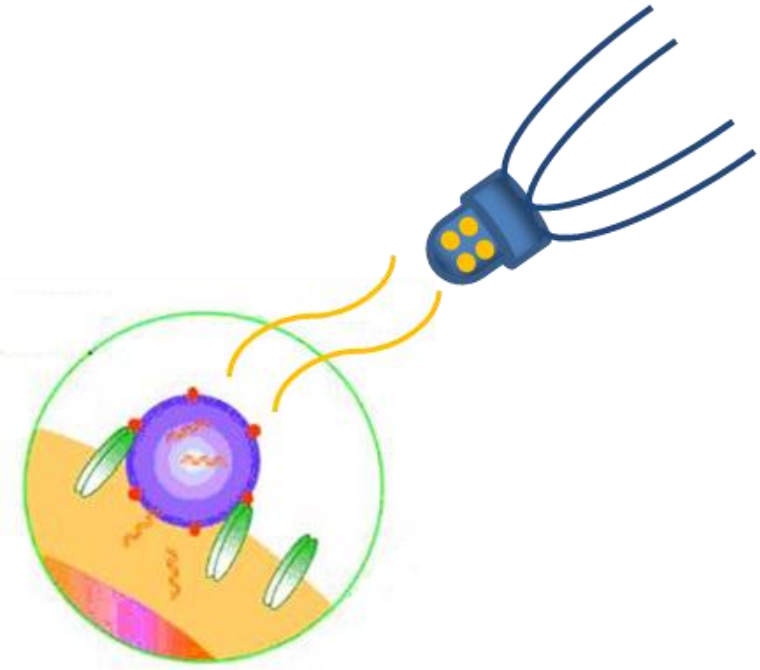


Figure 1.1.1 A schematic illustration of nano-roboot.

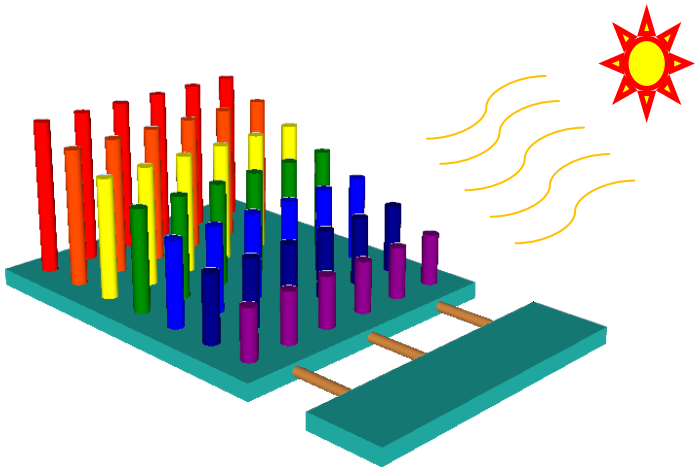


Figure 1.1.2 A schematic illustration of Solar cell.

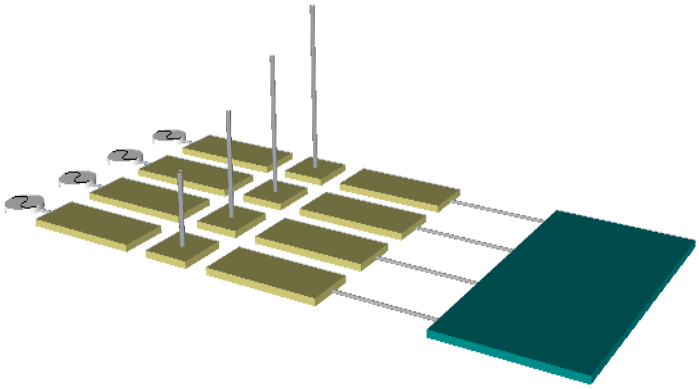


Figure 1.1.3 A schematic illustration of nano-optical antenna array.

In this thesis, main subject is to grow a vertical aligned and various heights CNT using e-beam lithography and PECVD technology. The growth condition of carbon nanotube about tip and root growth model by using PECVD was already reported by other teams [4, 8-9]. However, there are no data about multi heights carbon nanotubes on a substrate. Therefore, the purpose of this work is to grow CNTs which have different lengths at specific points.

To grow multi-walled CNT (MWCNT) on selected position, the patterned Ni catalyst by e-beam lithography and plasma enhanced chemical vapor deposition (PECVD) growth process were used.

1.2 Nano-optical Antenna

General antenna is a part of electronics device coupling between electromagnetic wave and electrical signal. According to Maxwell equation, there must be a time-varying current or an acceleration of charge to create radiation. Curved, bent, discontinuous, terminated wires can create charge acceleration. Periodic charge acceleration or time varying current is also created when charge is oscillating in a time-harmonic motion. There are several antenna parameters such as radiation pattern, directivity, gain, impedance, bandwidth, and etc. Beam pattern or radiation pattern which generated directivity appears antenna's radiation as a graphic data. The use of the electromagnetic wave toward certain direction and location has same meaning. The physical meaning of beam pattern plots graph about electric field strength toward all direction at antenna. Antenna is classified by the type of radiation pattern. Isotropic antenna is an ideal antenna that can radiate to all direction with equal power and has certain radiation pattern. Omnidirectional antenna has a certain radiation pattern at a plane. The shape of radiation pattern looks like doughnut shape. The figure 1.2 shows the radiation pattern of dipole antenna. An important antenna property element is that how much energy can focus on a certain direction. This property of antenna is called directivity. The directivity is equal to a power gain when the efficiency of antenna is 100 percent. Normally the gain of antenna is a relative value comparing with reference antenna. For connecting two elements in order to maximize the power transfer and minimize reflections, impedance matching is required. The antenna changes properties depending on its geometry particularly radiation pattern. The common antenna is dipole antenna. For satisfying resonance frequency, the physi-

cal length of antenna is half of wavelength bending conducting wire with different pole. The dipole antenna has Omni-directional beam pattern. Monopole antenna is also common. While monopole antenna seems like dipole, the ground replaced one conducting wire. The ground operates like conducting wire by the imaging effect. Therefore the length of antenna is quarter of wavelength instead of half-wavelength. Due to the length of antenna determining the antenna property, the length is very important parameter to make an antenna. When the frequency is a THz range, the physical length of antenna has to be micro or nano scale. Therefore nano-antenna is essential as a THz communication. [15]

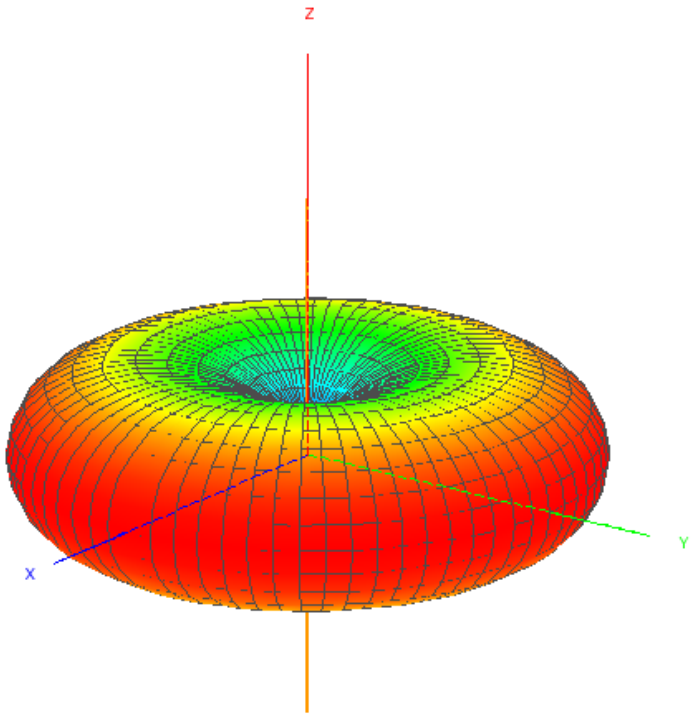


Figure 1.2.1 A radiation pattern of dipole antenna.

Optical or nano antenna is a device to convert light to electrical energy. Nanostructure can apply this phenomenon like an antenna. A receiver interacts with free optical radiation and it is ideally quantum absorber such as an atom, ion, quantum dot, and defect center in a solid. An optical antenna sends the information with extremely high data rate due

to fast modulation from the wavelength of high frequency with small energy. Several types of optical antenna have researched. The early step of optical antenna, the nano size gold particle for localizing optical radiation on the surface of some sample is the origin of it. This gold nanoparticle, optical antenna, applied to the spectroscopy technology especially the metal tip of it. Next the bow-tie antennas were developed for near field lens probes. The bow-tie antenna improved the directivity more than gold nano particle. The Yagi-Uda antenna using five array of gold nano rod with improvement of the directivity was developed. The Yagi-Uda antenna made by five gold nano particles consisted of a reflector, a feed, and three directors. Through these three researches, optical antenna improved the directivity with having a resonance frequency and the structure difference also affect to the radiation pattern of nano antenna like traditional antenna. [15]

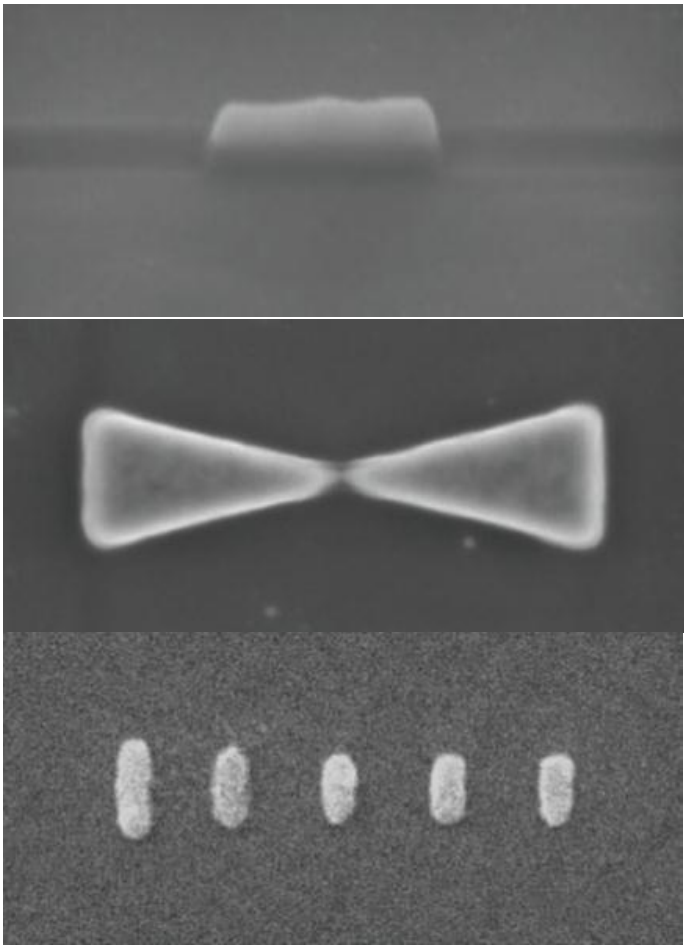


Figure 1.2.2 SEM images of nano antenna. [2]

In case of the visible light, the wavelength is THz and structure is totally different comparing with existing antenna structure. However, nano-structure partly applied the antenna concept to catch the visible light. When the light penetrates a hole, intensity of transmitted light reduced with decreasing hole's diameter. In contrast tradition theory, certain wavelength strongly couple hole like antenna even the strength of passed light is bigger than the amount of incident light when the hole size is decrease to the nano size. The size of hole is smaller than wavelength. Variety of unexpected optical properties such as strong enhanced transmission and wavelength filter was appeared. This phenomenon is occurred by the interaction between light and surface of the metal. Nano structure such as single apertures, periodic corrugations, and array of hole was operated like an antenna. They can control the light by changing periodic groove or changing the distance among nano dot pattern. [12]

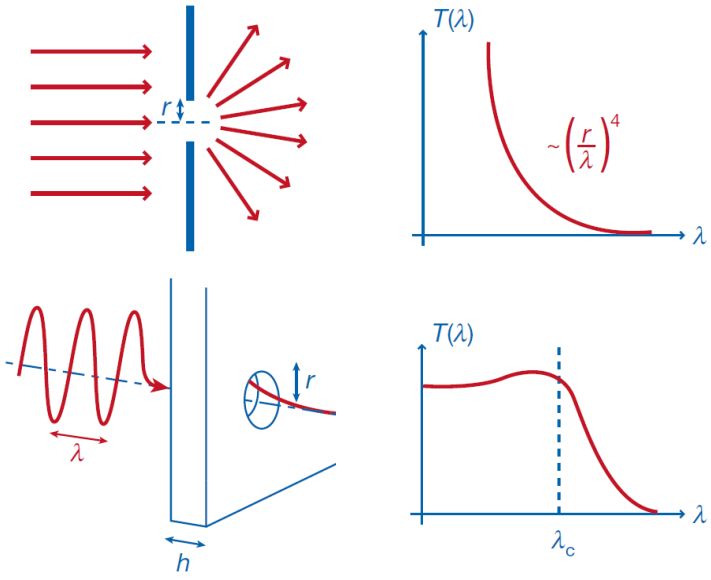


Figure 1.2.3 Two schematic illustration of nano structure and its property. [12]

1.3 Carbon nanotube

Carbon nanotubes have great interest since it was discovered by Dr. Sumio Iijima of the NEC Corporation in 1991. Cylindrical shape consisted of graphene sheet from hexagonal carbon bonding. Due to their electronic and extraordinary mechanical properties such as ballistic electron transport and large elastic modulus, Carbon nanotube has been researched widely in these days. In addition, carbon nanotube not only has electronic property, good current flow like Copper, but also appears the strength similar to diamond. The weight of CNT is light due to the vacancy inside the cylinder. A lot of outstanding advantages between electronic and mechanical properties, carbon nanotube was tried to apply many fields such as NEMs, transistor, display device and etc.

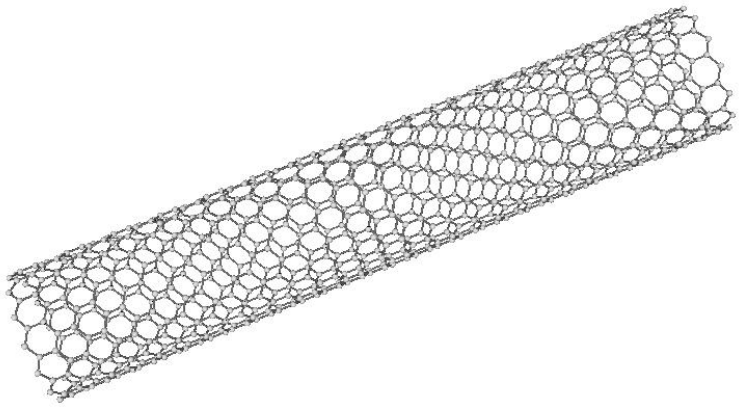


Figure 1.3.1 A schematic illustration of Carbon nanotube.

The CNT distinguishes two types depending on wall number such as Single-Walled Carbon nanotube (SWCNT) ant Multi-Walled Carbon nanotube (MWCNT). SWCNT has a diameter usually a few nano meters and MWCNT's diameter sized between 10 and 100 nano meter. CNTs have a unique electrical property from the electronic band structure of graphene. CNT can be a metal or semiconductor due to the chirality of it. The cylindrical structure of a

CNT impose periodic boundary conditions on the electron wave function around the CNT's waist, and transport in a SWCNT occurs only along the axis of the CNT, making a CNT 1D conductor. The conductance through the CNT is ballistic for such CNT. An electrostatic field can couple to the potential of the tube and shift its Fermi energy from the valence band, into the gap, and further into the conduction band, modifying the CNT conductance. CNTs owe their mechanical properties to the strength of the sp^2 hybridized C-C bond. The two most important parameters characterizing the mechanical properties of a material are the elastic modulus E that describes the slope of the stress verse strain curve, and the tensile strength which describes the maximum stress that the material can endure.[5]

The growth proceeds according to the following sequence of steps and one or more of these steps may be rate controlling, which varies from case to case and requires careful experimental analysis:

a) Diffusion of precursor through a thin boundary layer to the substrate.

b) Adsorption of species onto the surface.

c) Surface reactions leading to film growth.

d) Desorption of product species.

e) Diffusion of species through the boundary layer into the bulk stream.

The plasma gives the energy to grow Carbon nanotube and make low temperature possible. A hydrocarbon such as Acetylene adsorbed onto the catalytic particle surface releases carbon upon decomposition which dissolves and diffuses into the particle. When a supersaturated state is reached, carbon precipitates in a crystalline tubular form. There are two different Carbon nanotube growth model. One is Root growth model. If the particle's adhesion is strong, then the particle stays on substrate and grows the carbon nanotube on the par-

ticle. Another is tip growth model. In cases where the particle attachment to the surface is weak, then carbon precipitation occurs at the bottom surface of the particle and the filament lifts the particle as it grows. [4]

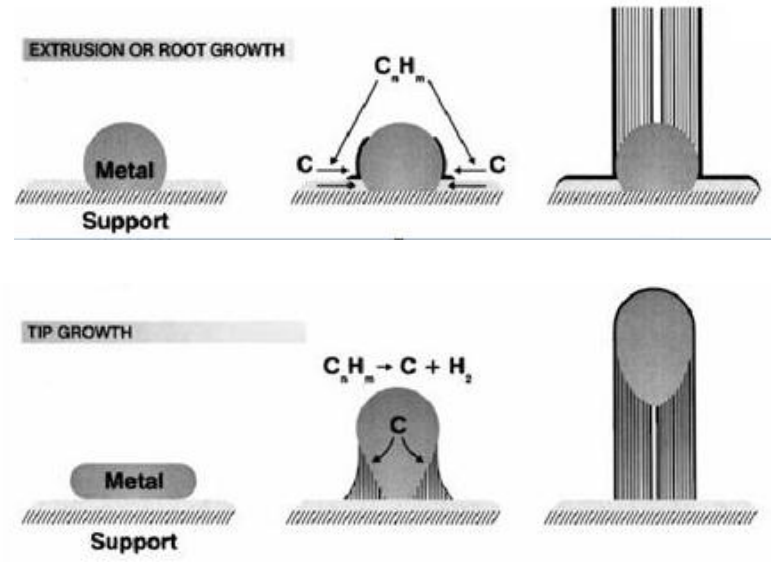


Figure 1.3.2 Two schematic illustration of Carbon nanotube growth model. [4]

Ⅱ. Experiment

The fabrication process of Carbon nanotube involves E-beam lithography, Photo lithography, Physical Vapor Deposition (PVD), lift-off, and Plasma Enhanced Chemical Vapor Deposition (PECVD) techniques. Scanning Electron Microscope (Hitachi S4800) is used for catalyst and CNT analysis.

2.1 Catalyst Pattern

There are two types of catalyst sample: Si-SiO_2-Nb-Ni and Si-SiO_2—Ni. In case of Si-SiO_2-Nb-Ni catalyst sample, the substrate was used p doped (100) oriented commercial silicon wafer with 1000Å thickness oxidation layer. For the antenna application either p type or n type silicon wafer can use for further fabrication. Dopant of prime grade silicon wafer is boron and thickness is in between 660-690μm. Samples cut out 1.5cm × 1.5cm for loading it on the e-beam lithography cassette and PECVD sample holder. About 1500Å Nb was deposited by sputter as an electrode. We tested the thickness of Nb layer with photo lithography pattern measured by the α-step. The chamber pressures is 1×10^{-6} torr to get high purity thin film layer and increasing pressure 5×10^{-2} torr with injection of 40sccm Ar gas flow for preparing plasma. A RF 200V plasma voltage was applied with 10rpm rotation for uniformity of Nb layer. The process pressure 1×10^{-2} torr was used for controlling deposition rate. The purity of Nb target is 99.95%. E-beam evaporator was used to deposit Nb layer.

The pattern design made by MyCAD and exported to the GDS Ⅱ file for e-beam lithography. The most important factor to be considered in the design is the pitch between catalysts and diameter of catalyst. Small distance between two catalysts can cause the cata-

lyst integration during CNT growth. Two types of array patterns were designed for catalyst. First, pattern designed for the statistical analysis and state of CNT growth. The 10 by 10 arrays from 200nm to 10nm of catalyst design were located on sample. Another array consisted of different diameter from 1um to 10nm proving a single CNT growth below certain catalyst diameter. After finishing design, GDS Ⅱ file converts to v30 in e-beam lithography control computer. A rearrangement of array is determined by JDF and SDF file. These files have information of current, location of array, sample size, dose and acceleration voltage.

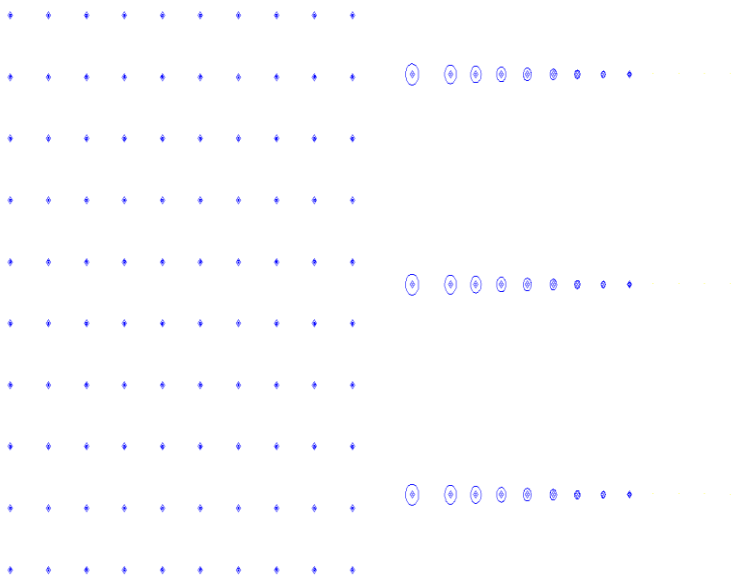


Figure 2.1.1 MyCAD design for catalyst consisted of 10×10 array and different diameter dot pattern.

JEOL JBX 9300 was used for the e-beam lithography for nano pattern. The sample has some cleaning process for preventing unexpected particle. The resist of E-beam lithography used polymethyl methacrylate (PMMA) A3 for the positive resist with 950 molecule weight. Electron beam resist is a material that is sensitive to high energy electrons and most

commonly used as a high-resolution resist for direct-write EBL. The resist is composed of long molecular chains suspended in a solvent. This PMMA A3 can be coated on a wafer using spin coating. Spin coating was done 5000rpm for 40 seconds with expectation of 90nm thickness e-beam resist. The spin speed and time determine the thickness of the resist on the sample. Soft baking heats up to 170℃ for 300 second and loading the sample. Calibration progress was operated for compensation of beam distortion, beam diffraction, height of sample, current, and etc. To get optimal condition, E-beam exposure is carried out with different doses and a 1nA beam current using 100 keV E-beam lithography system. The dose varied from 300 to 100μC/cm^2. Dose can effect about the size of the pattern. The current has trade-off between resolution and writing time. Although smaller current take much longer exposure time, it can get much higher resolution. The substrate was developed by a solution that is consisted of Methyl isobutyl ketone (MIBK): IsoPropyl Alcohol (IPA) = 1:1 for 3min and rinse with IPA in 30 second. Although there are two options agitation and ultrasonic for develop process. After developed e-beam resist, the Ni was deposited as a catalyst for Carbon nanotube growth using thermal evaporator with 0.5 Å/s deposition ratio. Low deposition ratio makes Ni layer much uniform. Lift-off, the sample puts into the acetone three hour. The sample puts into the acetone again and repeats earlier process three times or more. Finally, sample is cleaned by acetone and IPA for 30s for each. We made a catalyst using e-beam lithography for the selective CNT growth on a certain location.

For another Si_SiO2_Ni substrate, n-doped (100) Silicon wafer was used. The substrate coated a thin SiO2 layer by RF-sputter about 10nm. The SiO2 layer prevents the diffusion of the silicon to catalyst layer during heat-up process in PECVD. E-beam lithography is not easy to oxide layer on the top of sample for nano pattern due to the electron charging in oxide layer and it interrupts the electron bombardment from electron gun. But electron can penetrate little thickness oxide layer. Therefore we did E-beam lithography

pattern even the top layer is oxide. Lift-off process and other process are same as the Si-SiO2-Nb-Ni sample.

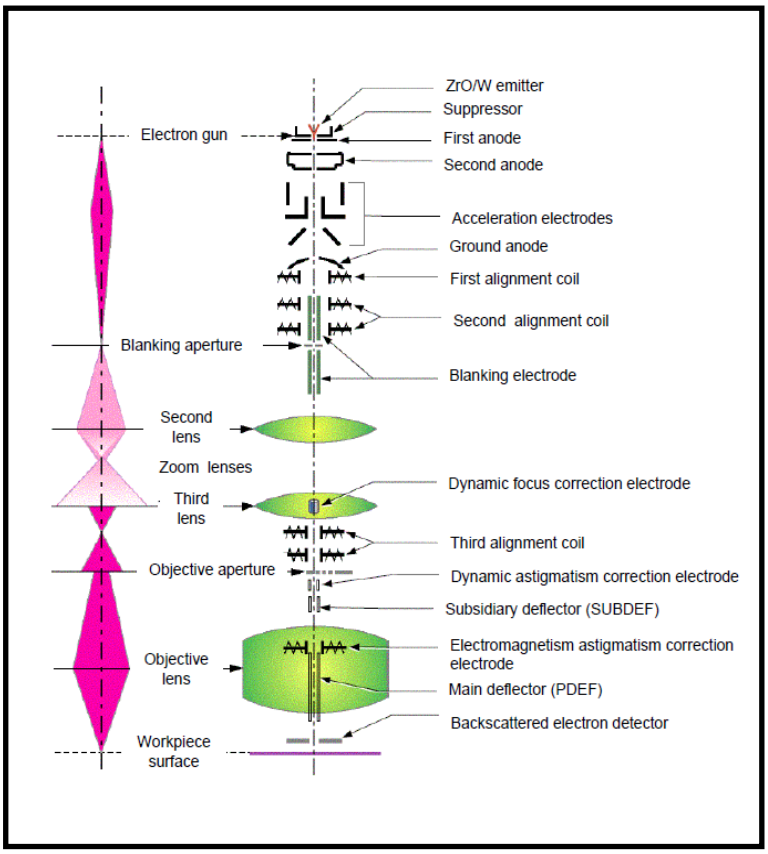
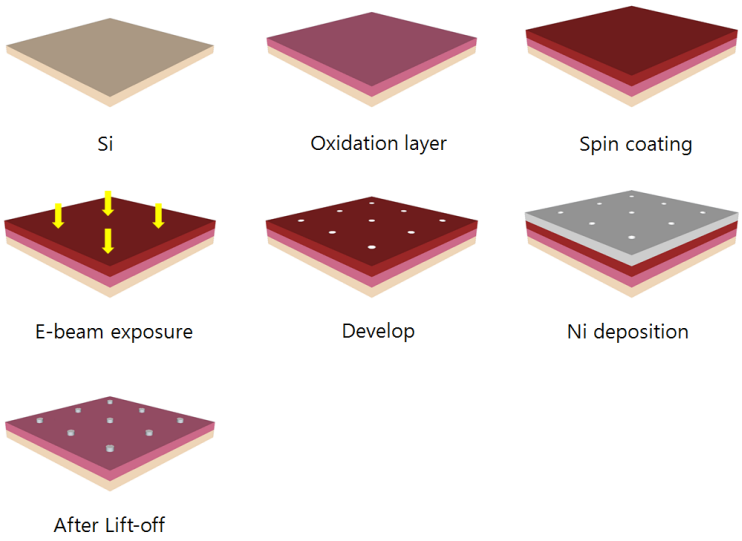


Figure 2.1.2 A schematic of E-beam lithography.

Si_SiO2_Ni Sample



Si-SiO2-Nb-Ni sample

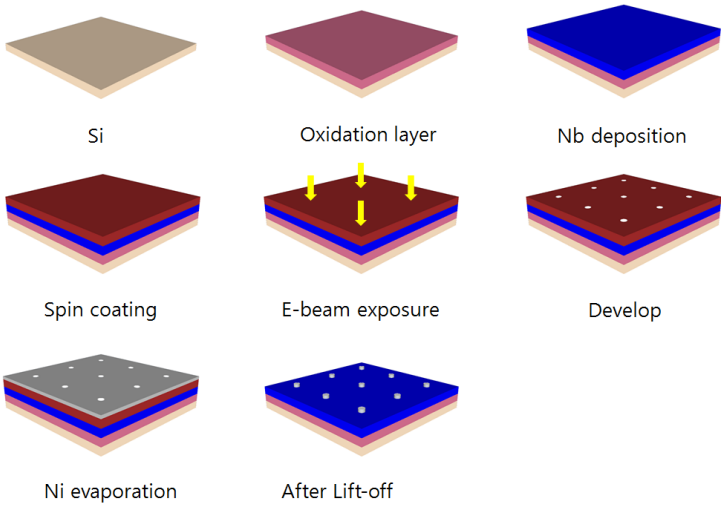


Figure 2.1.3 The fabrication process of catalyst using E-beam lithography.

2.2 Carbon nanotube Growth

For CNT growth, several catalysts such as Ni, Co, and Fe can be used. The Fe is usually as a catalyst for thermal chemical vapor deposition and Ni is best for plasma enhanced chemical vapor deposition. Before deposit Ni layer, we deposit oxide layer for preventing diffusion from silicon. Then deposited Nb layer is not only electrode coupling from antenna to other analysis equipment for further experiment after make nano-antenna. E-beam lithography is essential to make different size of catalyst at certain point. PECVD(Aixtron BlackMagic) is recommended for vertical aligned Carbon nanotube growth with DC plasma or AC pulsed plasma.

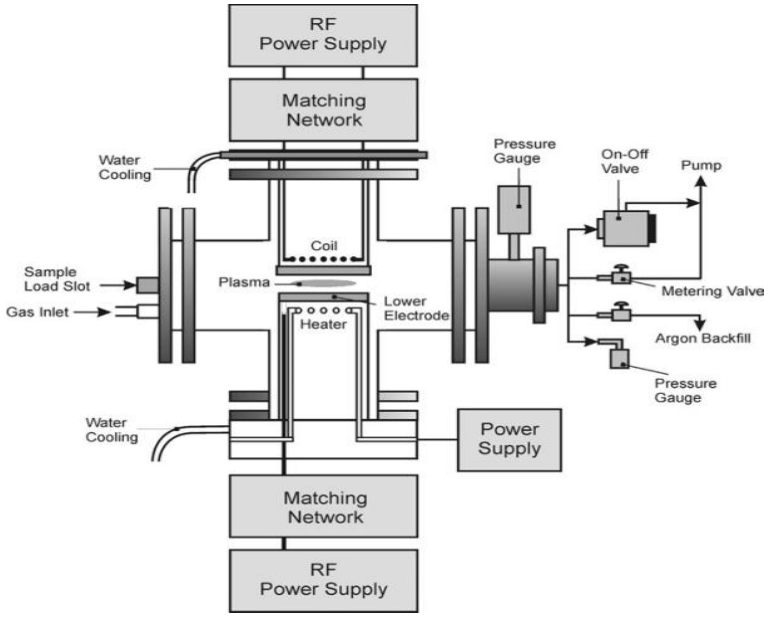


Figure 2.2.1 A schematic of PECVD. [4]

Because of the uncertainty of thermal distribution, sample exactly loaded on the center of sample holder. When the chamber pressure was below 2×10^{-1} torr 200sccm NH_3 gas was injected with controlling pressure at 6 mbar. The NH_3 gas prevents the oxidation of catalyst during heating process and gives etching effect for unstable C-C bonding for CNT growth. The sample holder heated up until 550℃ with heating rate 50℃ per minute. Gradu-

ally heating up process can give enough energy to the catalyst melting and to form single catalyst. Waiting 5seconds after injection of C_2H_2 65sccm for CNT growth and sample is heated up again up to 560℃ for 55seconds. After finishing this process, plasma power is applied and heat up the chamber at 650℃~750℃. The growth time is 10 minutes. Before unload the sample, sample is cooling down for 1hour. N2 gas is injected for the safety from toxicity.

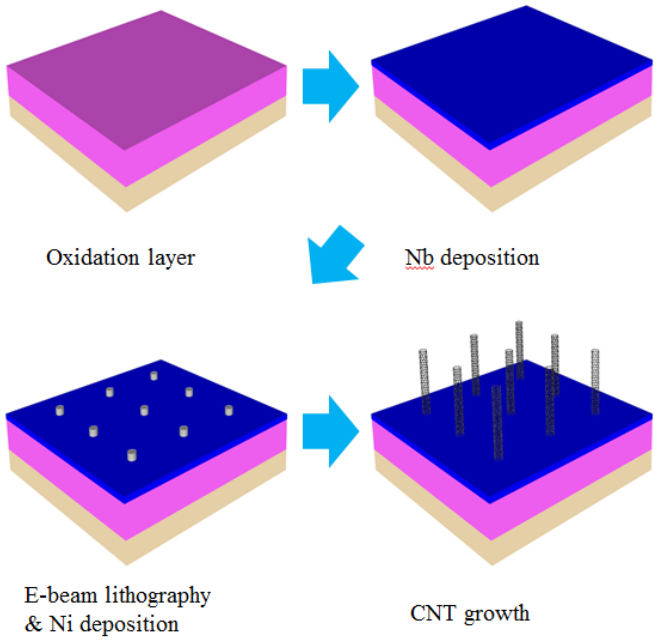


Figure 2.2.2 Growth process of the CNT.

Ⅲ. Result

3.1 Nano patterned Ni catalyst using E-beam lithography

To form catalyst for single CNT growth, it is essential to make a dot pattern with nano meter size. There is a size deviation between E-beam lithography patterns and the designed values. Dose the amount of the electron at the exposure area is an important parameter to optimize the catalyst pattern size. Usually, a catalyst from high dose condition is bigger than that of small one. At the first dose test, the negative type e-beam resists were tested using Man-2401 and Man-2403. The difference of two resists is viscosity. So that film thickness is around 100nm and 300nm at 5000 rpm coating condition. The catalyst pattern size was varied 10nm to 1000nm. Figure 3.1.1 and figure 3.1.2 are the dose test results. In dose test result about Man-2401, all catalyst sizes are bigger than the designed sizes. It is hard to get the pattern below 200nm in the dose test result using Man-2403 e-beam resist.

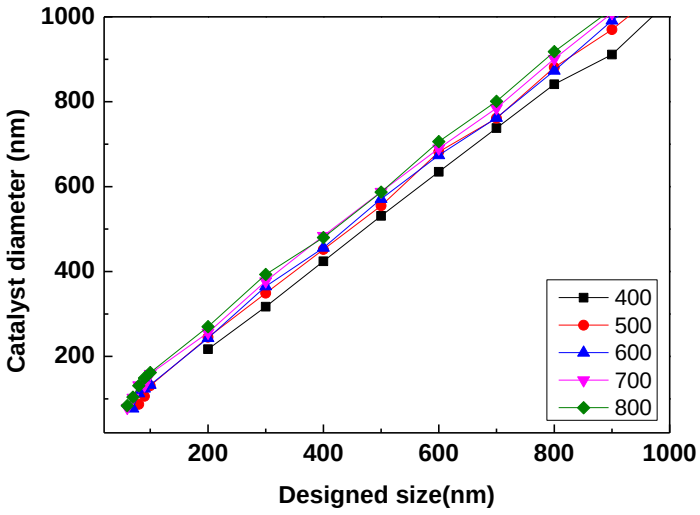


Figure 3.1.1 Negative dose test result from Man-2401.

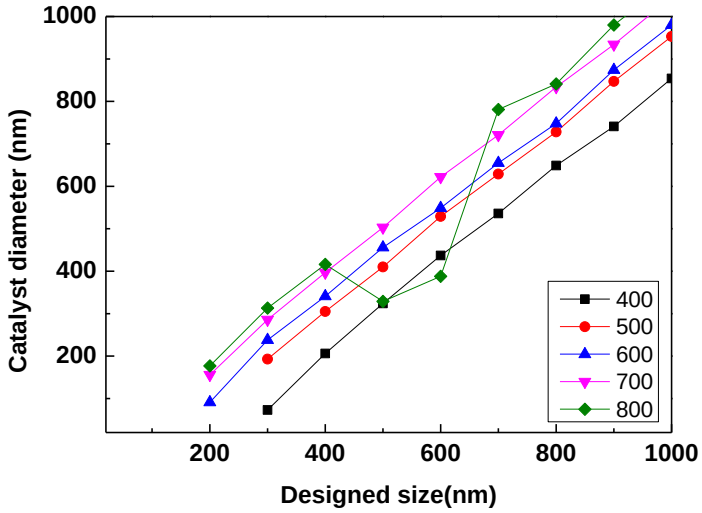


Figure 3.1.2 Negative dose test result from Man-2403.

The positive PMMA A3 was used for dose test as well. Three substrates, ITO, Nb, and Mo, were tested to find optimal material about catalyst pattern. The ITO dose test result shows the biggest patterns compared to the designed size due to the high secondary electron yield rate to PMMA. (Figure 3.1.3) In the test on the Nb and Mo substrates, some dose condition make good matching points between design size and real size at each catalyst diameter as shown in figure 3.1.4 and figure 3.1.5. Through these dose tests, we set up the optimal dose for each catalyst size and bottom layer. We chose Nb as a bottom layer due to a proper dose range and melting point. Optimal dose for each pattern size on Nb is shown in figure 3.1.6. The dose is increasing with decreasing catalyst pattern. Smaller pattern needs higher dose condition. We design the dot pattern from 200nm to 10nm. hoever, there is no pattern result below 20nm. We have two assumptions analysis. One is the difficult to distinguish between small nano pattern and bottom morphology although it is formed on the substrate. Another, there is no dose condition below 20nm. Due to the mismatching of dose condition, the catalyst pattern below 20nm appears at high dose condition and it is bigger than design size.

After 3 minutes developing process in ultrasonic system, Ni was evaporator and the Ni catalyst was formed after the lift-off process. There are two shapes of Ni catalyst design, circle and square, however both of them are show almost circle pattern below 100nm. SEM image of fig. 3.1.8 shows the different catalysts from 30nm to 200nm.

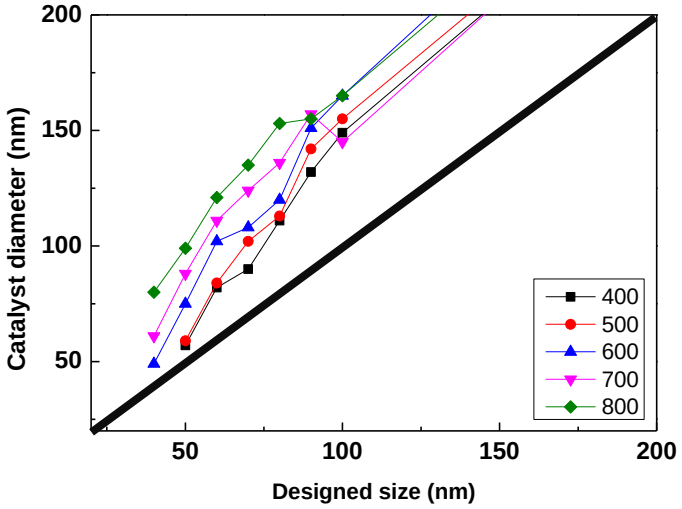


Figure 3.1.3 Positive dose test result on ITO layer using PMMA A3.

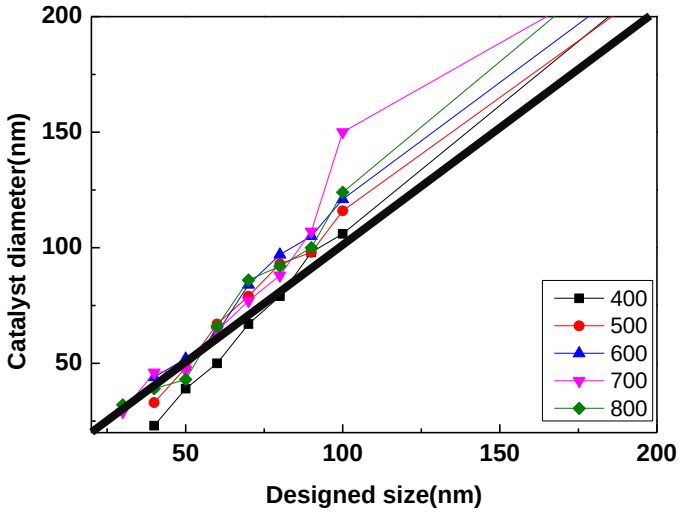


Figure 3.1.4 Positive dose test result on Mo layer using PMMA A3.

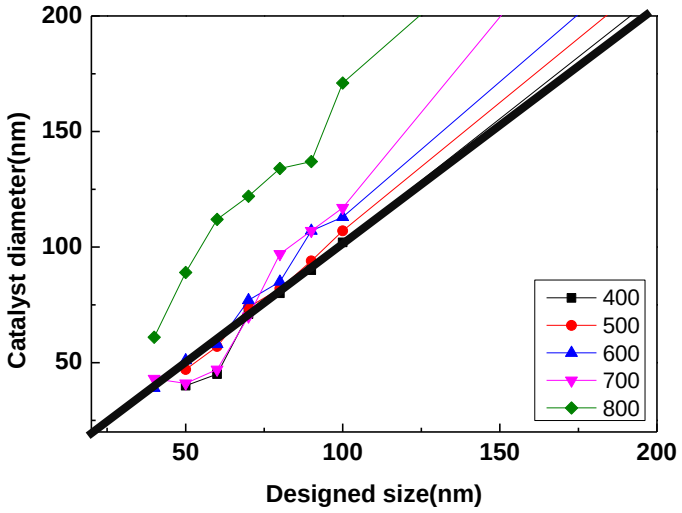


Figure 3.1.5 Positive dose test result on Nb layer using PMMA A3.

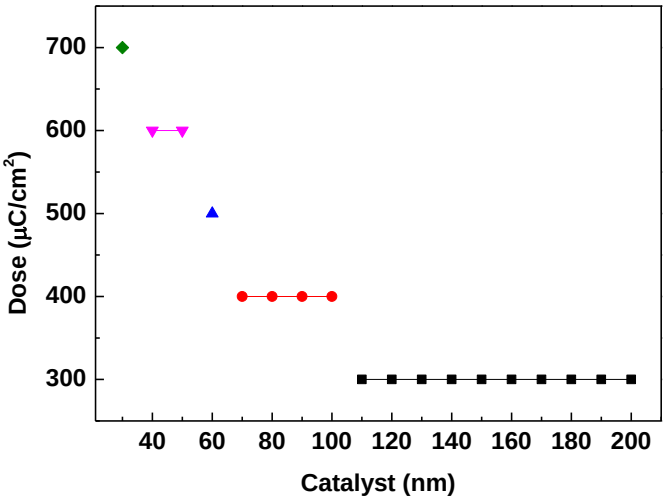


Figure 3.1.6 E-beam lithography result optimized dose condition for each catalyst diameter .

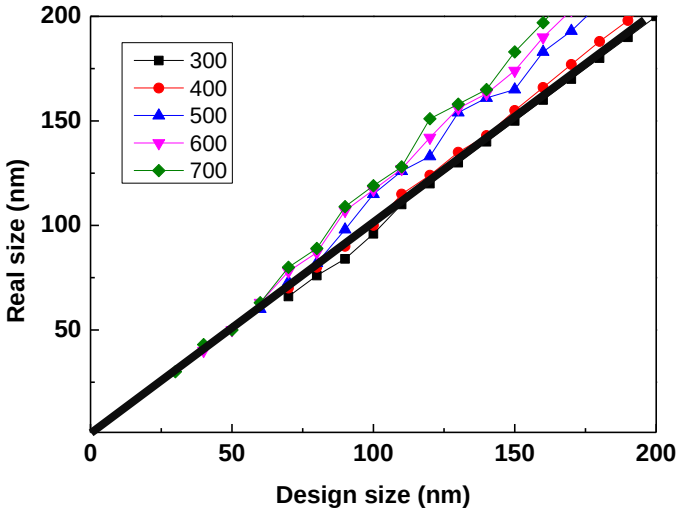


Figure 3.1.7 Size deviation between designs and real pattern.

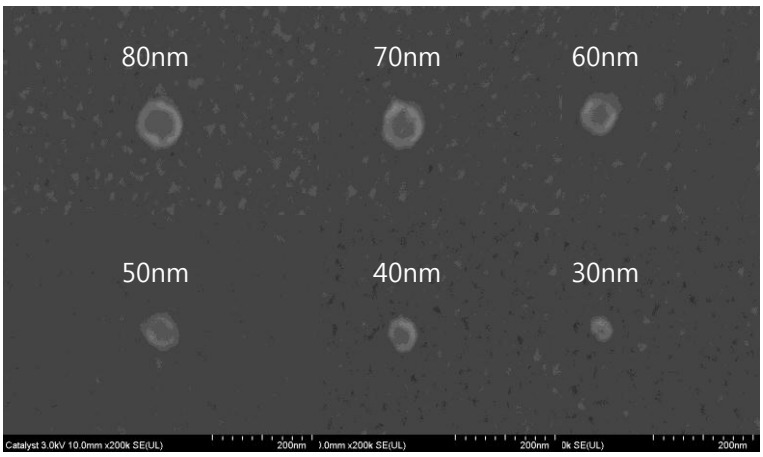


Figure 3.1.8 Catalysts sized 80nm to 30nm.

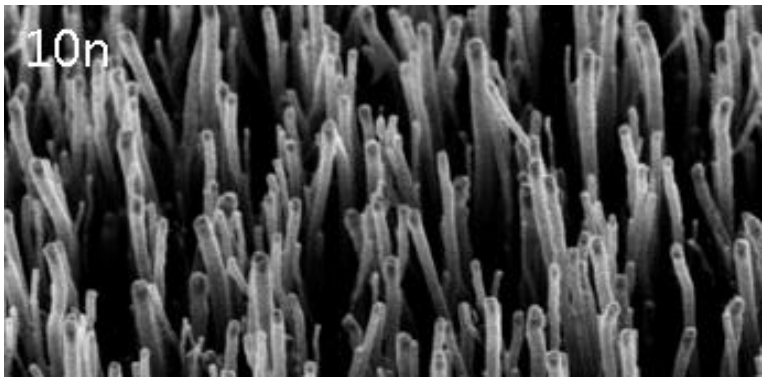
3.2 CNT growth parameters

The CNT growth is depended on several parameters such as pressure, plasma, heating, and gas flow. We did several experiments on whole Ni deposition sample to finding optimum condition for selective CNT growth due to high cost from e-beam lithography.

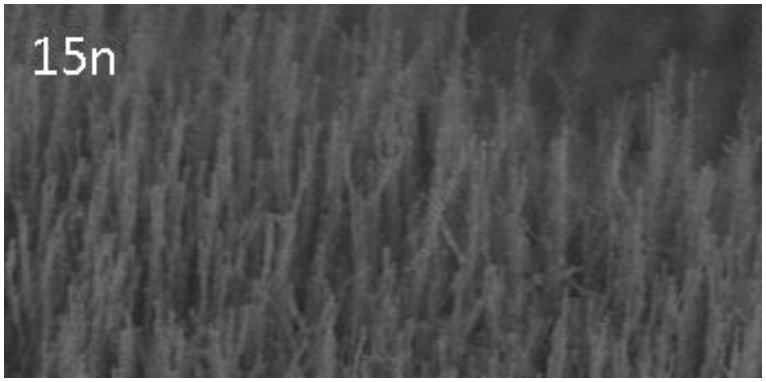
3.2.1Catalyst thickness

Thickness of catalyst can change the size of nucleation during heating of CNT process. Below 10nm catalyst thickness, CNT growth was curve. Thin catalyst thickness is same meaning to the little Ni volume. Small nucleation caused by thin Ni catalyst was damaged by etching effect. Above 10nm catalyst thickness, the CNT growth shows much straight than 7nm.

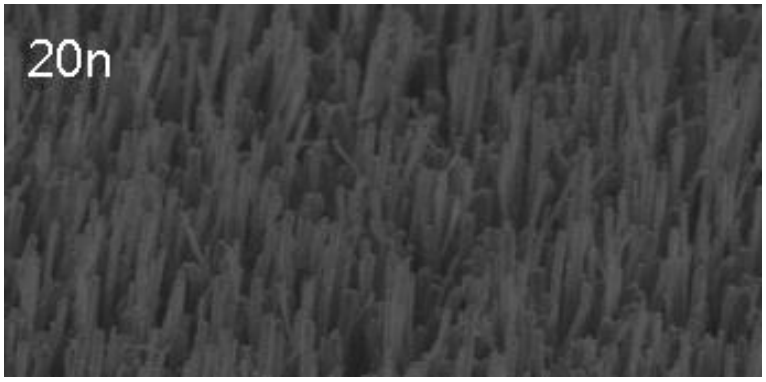
(a)



(b)



(c)

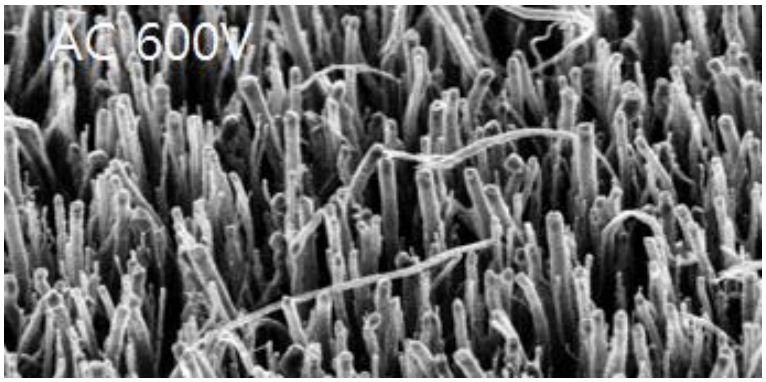


(d)

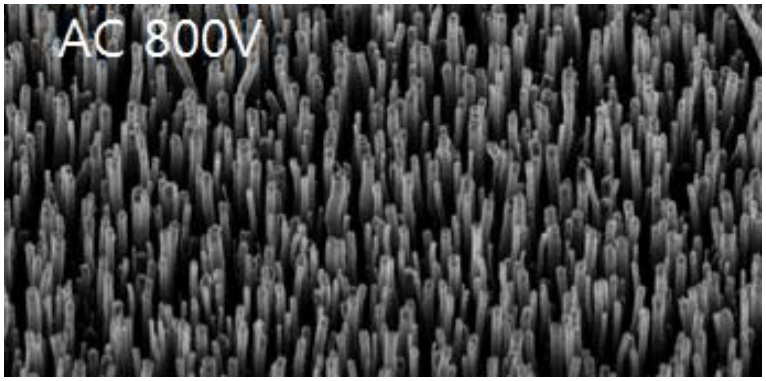
Figure 3.2.1 CNT growth from different catalysts thickness. (a)7nm, (b)10nm, (c)15nm, (d)20nm

3.2.2 Effect of plasma state

The one of the growth parameter is plasma state, which makes CNT more vertically aligned one and decrease process temperature because the positive ion bombardment of surface gives some energy for growth. Figure 3.2.2 and figure 3.2.3 are the SEM image of the AC and DC plasma growth with different plasma bias. Sample was included some serpentine CNT in AC plasma growth condition. From the test result, high plasma bias always shows the more straight CNT growth. Although DC 600V and DC 700V CNT growth appear vertically aligned CNT growth, we choose DC 600V condition due to the arcing at high plasma bias voltage. The arcing can damage the sample, even disappear CNT in worst case.

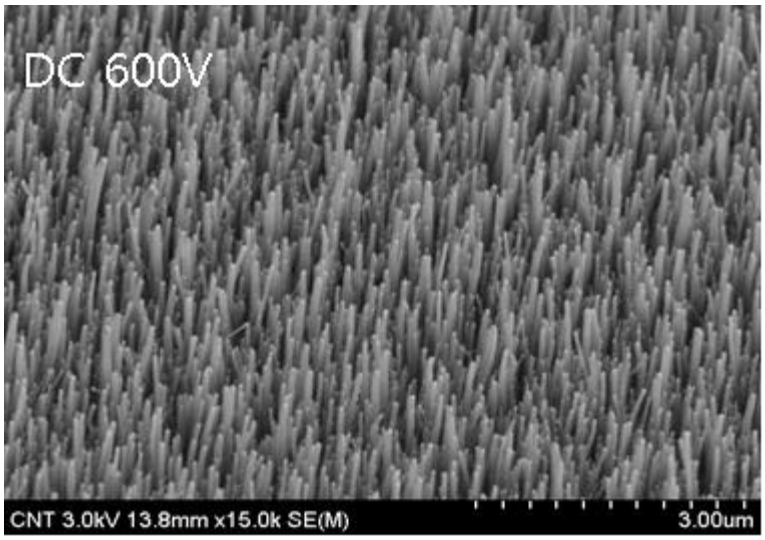


(a)

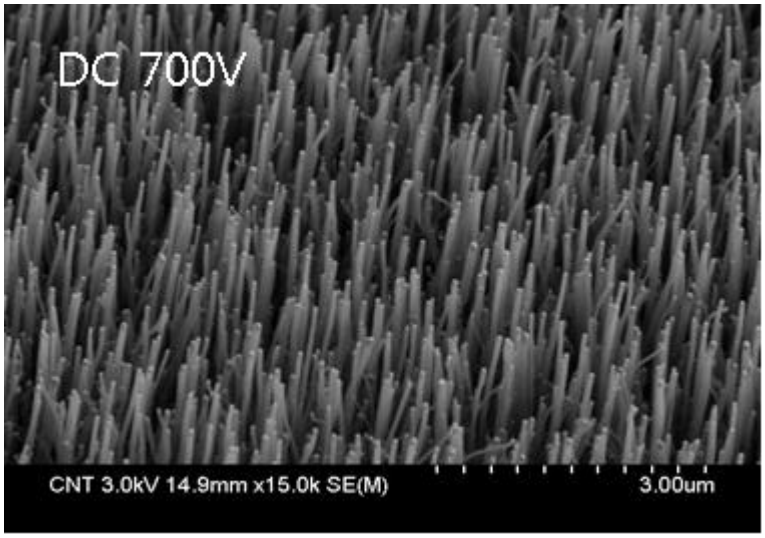


(b)

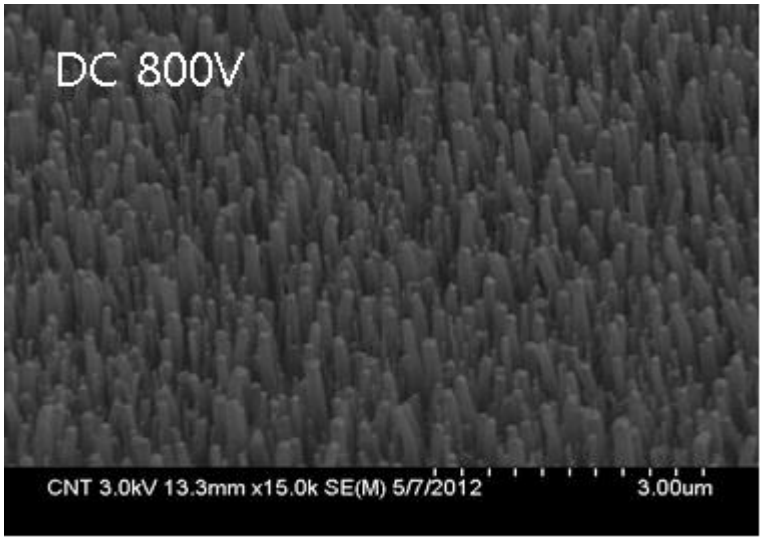
Figure 3.2.2 SEM image of AC CNT growth (a) AC 600V, (b)AC 800V.



(a)



(b)



(c)

Figure 3.2.3 SEM image of DC CNT growth (a) 600V, (b) 700V, (c)800V.

3.2.3 Process gas effect

We used two gases, acetylene and ammonia, for the CNT growth. Ammonia has a function to break amorphous C-C bonding and acetylene is a carbon source. The gas ratio between acetylene and ammonia affect to the shape of CNT. Fixing ammonia gas flow, acetylene was changed to find the relationship between carbon source and CNT. Figure 3.2.4 shows SEM image of CNTs grown at different C_2H_2 gas flow ratios. The parameters such as NH3 gas flow, pressure and the plasma voltage were kept constant at 200 sccm, 6mbar, and 600 V, respectively, while the C_2H_2 flow is changed from 35 sccm to 75 sccm which are gas ratios about: (5:1), (4:1), and (3:1). As shown in Figures 3.2.4 shows well-aligned Carbon nanotubes are grown from the same catalyst size. For 35 sccm or 45 sccm, CNTs are very thin and the yield of single CNT is low. The reason of CNT growth result at 75 sccm looked like pyramid is that enough carbon sources stacked at bottom of CNT. Therefore 55~65 sccm condition is fixed experimental. Figure 3.2.5 shows the length and thickness CNT data from different acetylene gas flow. The bottom thickness of CNT is proportional to the gas flow. The control of gas flow for CNT growth affects to the final shape specially diameter.

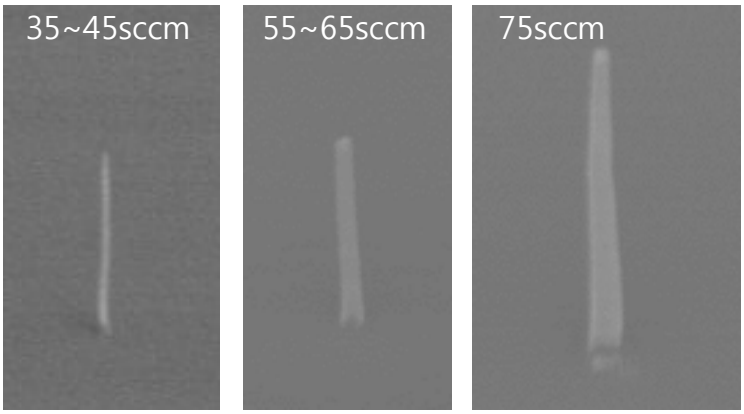


Figure 3.2.4 SEM image of CNT growth from different gas flow.

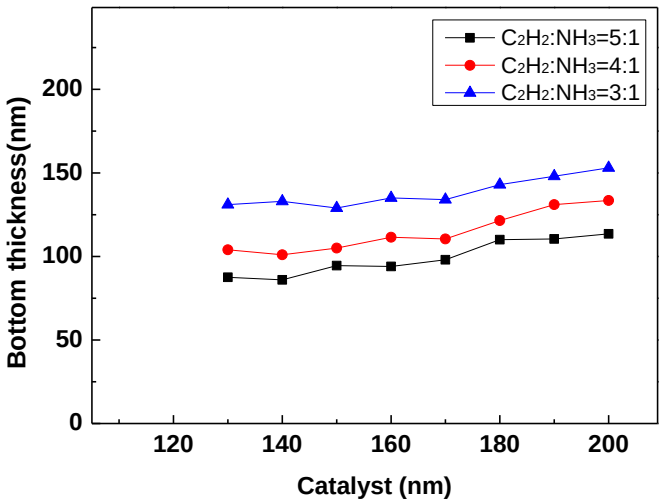


Figure 3.2.5 Bottom thickness data depending on gas ratio between ammonia and acetylene.

3.2.4 Temperature effect

Experimental results show the CNT diameter with depending on different temperatures and catalyst size. Below 500℃ Plasma state is unstable. At 600℃, we get well aligned CNT and we increased the temperature for further investigating from the thermal effect. In specific, we expected that the CNT growth will be more due to thermal energy when the temperature is higher. However the CNT growth up to 750℃ still shows vertical aligned state. At 650℃, CNT appeared well vertically aligned one than other temperatures because thermal energy, isotropic energy is lower than others during growth process. The temperature effects not only CNT height but also plasma power. The CNT shape at each temperature is totally different due to the relationship between temperature and plasma.

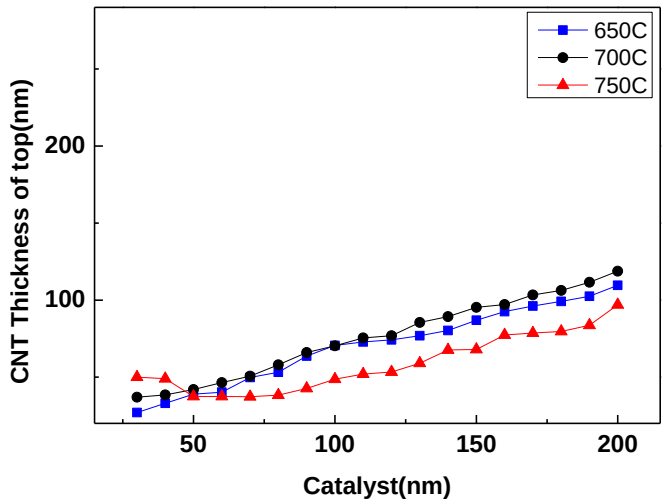


Figure 3.2.6 Top diameter of CNT depending on the temperature

3.3 Single CNT growth

For the Nano-optical antenna application, it is necessary to make a single CNT growth. Although it is hard to get a nano pattern below 30nm, we design the catalyst diameter among 1μm to 10nm. CNT growth states show with various diameter catalysts from 1μm to 60nm in figure 3.5.1. Below 60nm pattern, there are no CNTs because the small catalyst can be evaporated or oxidation easily during heating process. Above 300nm, the number of CNT is more than two due to the breaking of catalyst and nucleation during heating up the temperature. Below 200nm, single CNT is main state. With 10nm increment and 5μm pitch, a 20 nm thick Ni was patterned a circle dot with 10×10 array. Array of circle dots were patterned using electron beam lithography in which the width of the catalyst was varied from 1000 to 60 nm. Figure 3.5.1 shows the shape of CNT which were nucleated on these Ni dot array. Although the critical size for the nucleation of single CNT is 300nm, it is not always showing the single CNT growth even the size is below 300 nm. The single bar graph, figure

3.5.2, indicated the average number of single CNT growth. We choose catalyst size from 200nm to 10nm with considering CNT length and stable single CNT growth. There is no CNT growth between 20 and 10nm due to the problem from e-beam lithography process. We varied temperature 650℃ to 750℃ with fixed other growth condition. X axis of figure 3.5.3 shows the catalyst diameter and y axis indicated the number of single CNT growth. Each temperature show different result. The most important point of the counting graph is the number of single or two CNT growths. For All condition, the yield of the single CNT growth is decreased with decreasing catalyst size from 200nm. Near the 200nm catalyst, single CNT yield ratio is peak for every temperature condition. With decreasing catalyst size, the catalyst can be oxidation or etching by NH_3 gas during process. Therefore, the yield is dropped slightly. At 650℃, the graph shows the yield ratio above 80% at the catalyst size between 180nm and 200nm. To get a high yield ratio from small catalyst, the more careful control of the growth process is required. The yield of CNT growth between 100nm and 200nm is lower than 650℃ at 700℃ except CNT growth from small catalysts. The worst yield rate was appeared at 750℃ as shown in figure 3.5.3. Because high temperature can cause the oxidation or evaporation easily, the yield ratio is decreased even the catalyst condition of 180nm, 190nm, and 200nm.

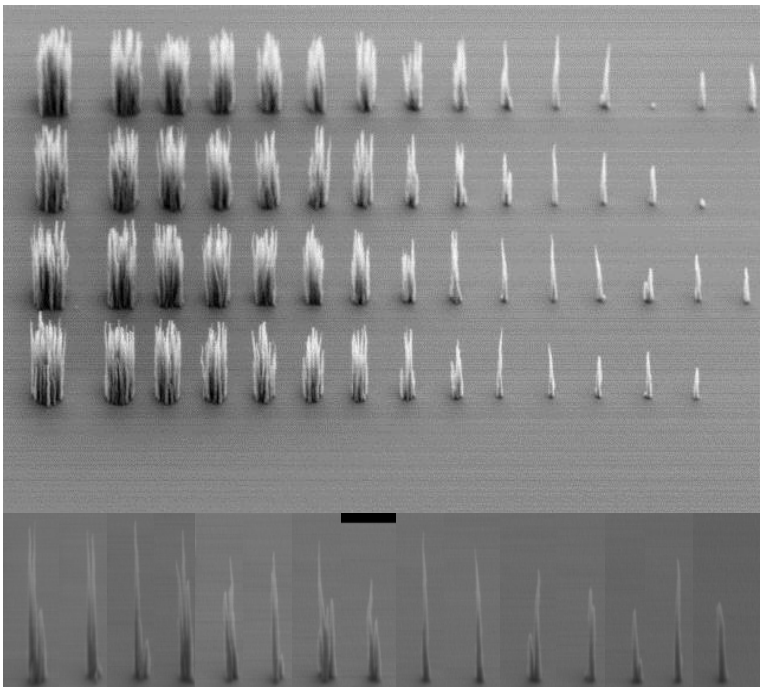


Figure 3.3.1 SEM image of CNT array from different catalyst diameter

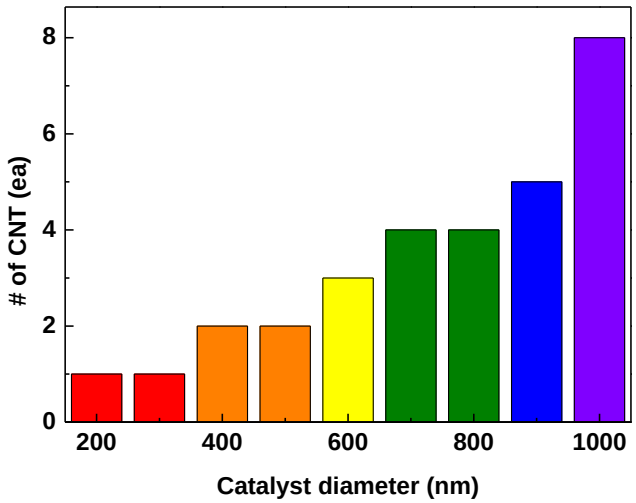
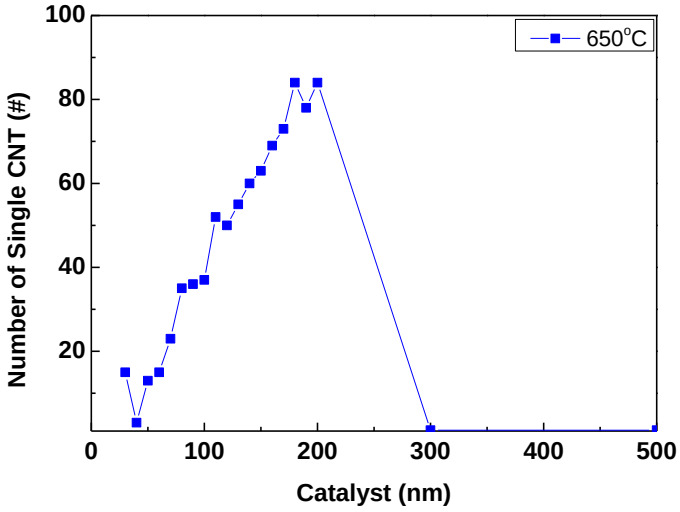
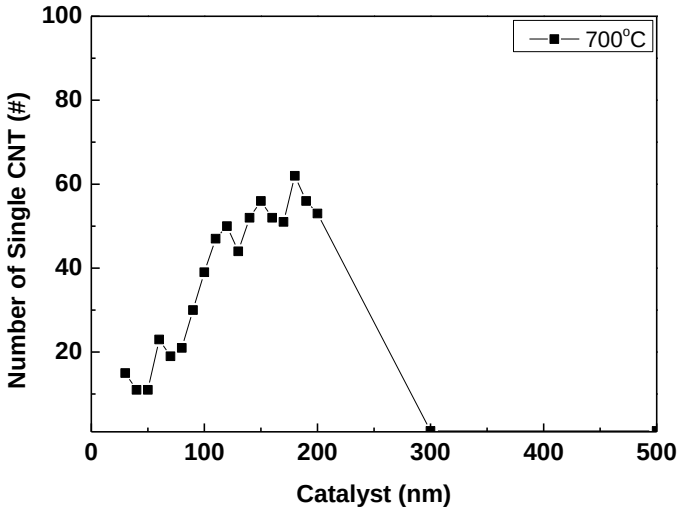


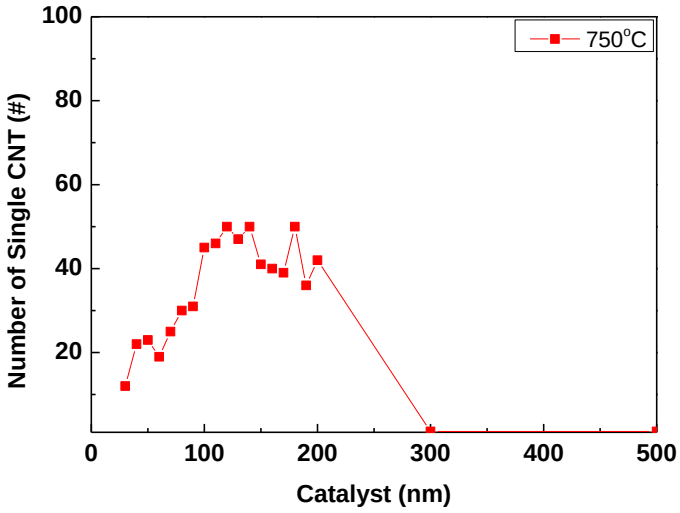
Figure 3.3.2 Number of Carbon Nanotube from different catalyst size.



(a)



(b)



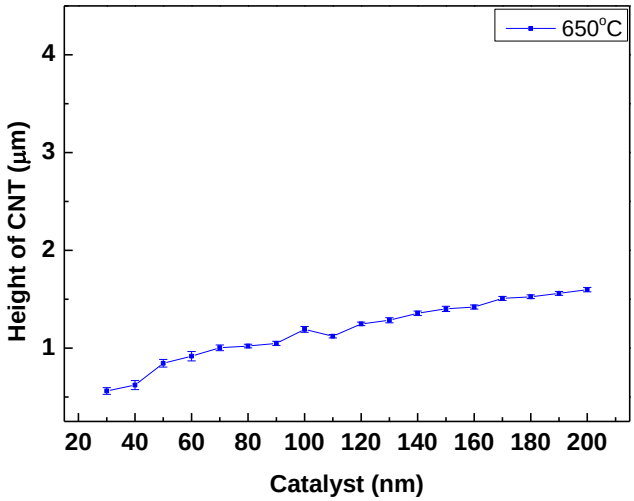
(c)

Figure 3.3.3 Percentage of single of two Carbon Nanotube growth for each temperature.

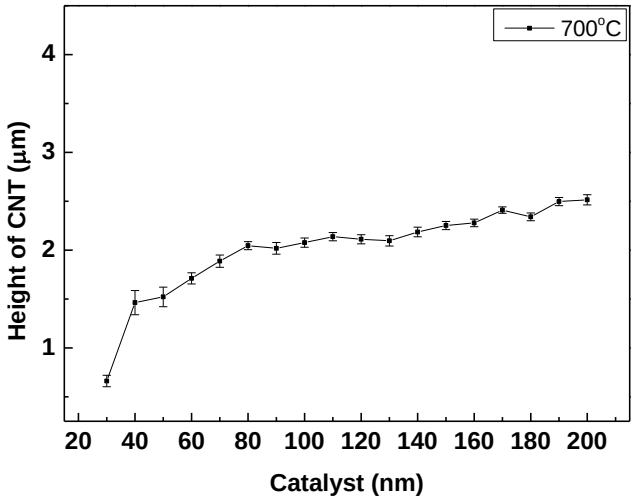
(a)650℃, (b)700℃, (c)750℃

3.4 The height of CNT

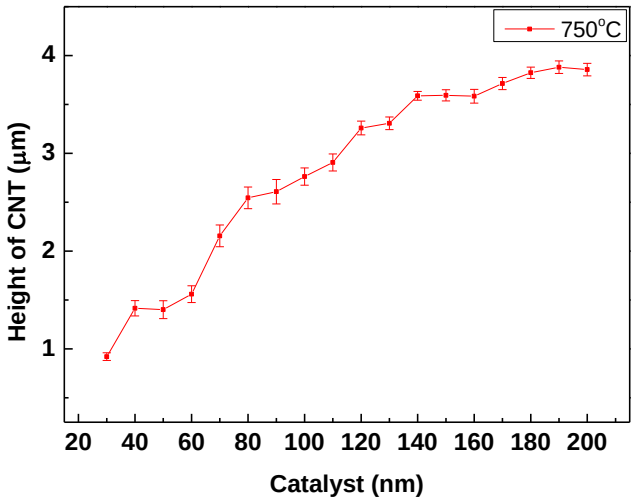
As mentioned earlier, the final target is multi size antenna structure considering diffusion rate of catalyst, the catalyst size gives some effect to the growth rate of CNT. CNT were grown different catalyst pattern at three different temperatures while keep other parameters constant. Following figures shows the CNT growth data at 650 ℃, 700℃ and 750℃. With increasing catalyst size, the CNT length is increased to all temperature conditions. The height of CNT tends to depend on the catalyst size in every CNT growth with different temperatures. Because of the size differences, the surface area of Ni is variety and affects to grow the CNT. In large diameter catalyst, the much carbon source can attach the surface of Ni catalyst. High temperature growth cause high length of CNT. We guess that high temperature has much more energy to give CNT growth. Although the CNT height from 30nm catalyst is almost similar for all conditions, the length deviation of CNT from 30nm catalyst and 200nm catalyst at 700℃ and 750℃ are bigger than 650℃ condition. In addition, the height deviation depended on catalyst size is increased at higher temperature process. The saturation points of CNT height are appeared different temperature. This data also analyzed by SEM image of the 10 × 10 catalyst array. The attached histogram data shows the distribution of CNT height at certain catalyst diameter. We choose three points to make histogram data. The histogram data was chosen CNT growth from the catalyst size 100nm to 200nm. It shows dramatically about the height change. From this data we prove that the various heights CNT array can be controlled by catalyst size and temperature for nano antenna. Mentioned earlier, the various CNT heights can couple different wavelengths. The 650℃ also show the best result for optimal size controlling due to the small deviation about height and histogram distribution.



(a)



(b)



(c)

Figure 3.4.1 Height of CNT with various temperature. (a) 650℃, (b)700℃, (c)750℃.

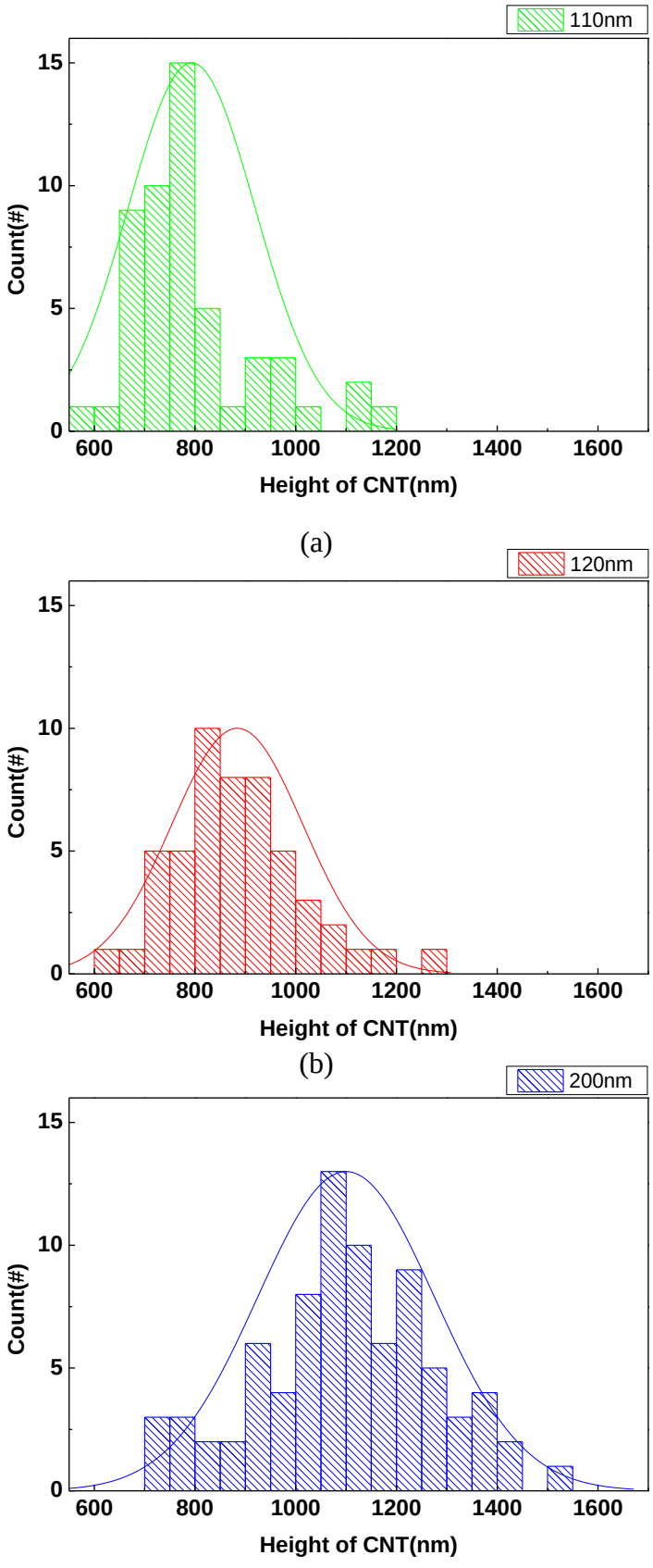
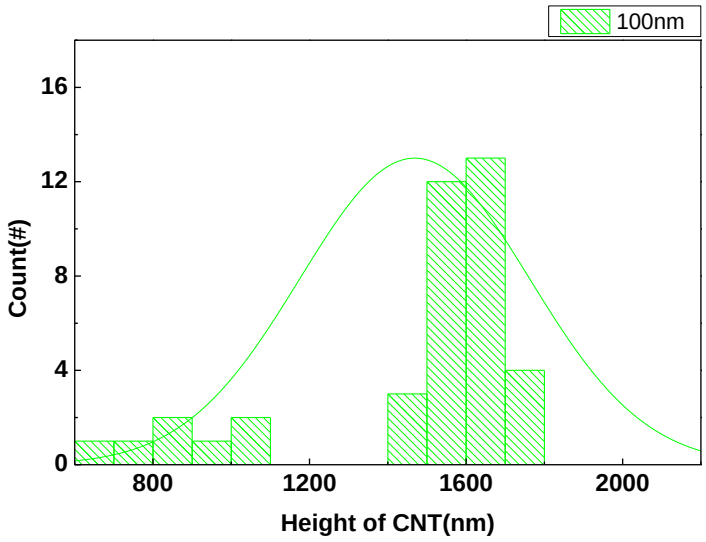
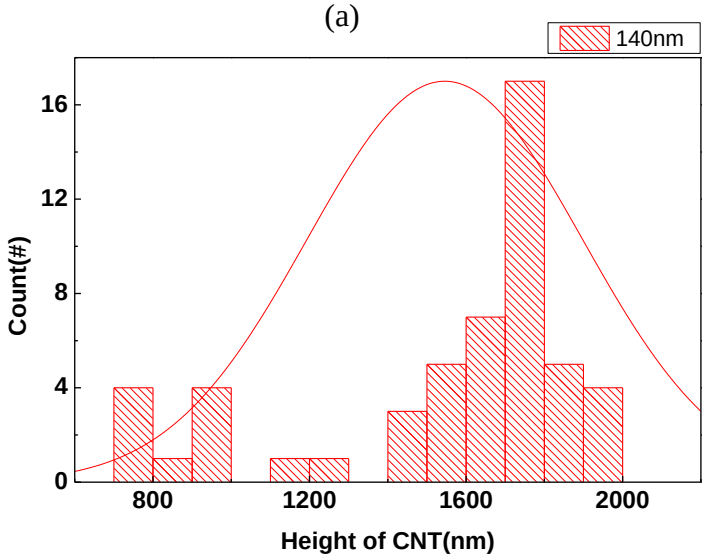


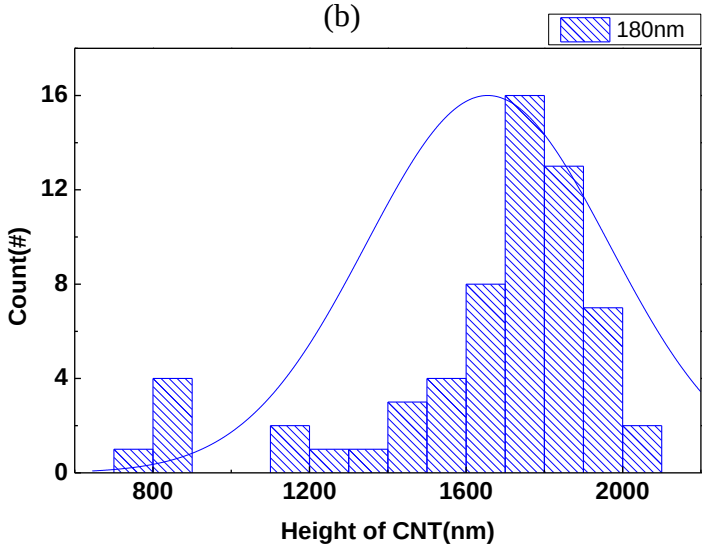
Figure 3.4.2 Histogram data of CNT at 650℃. Catalyst diameters are 110nm(a), 120nm(b), and 200nm(c).



(a)

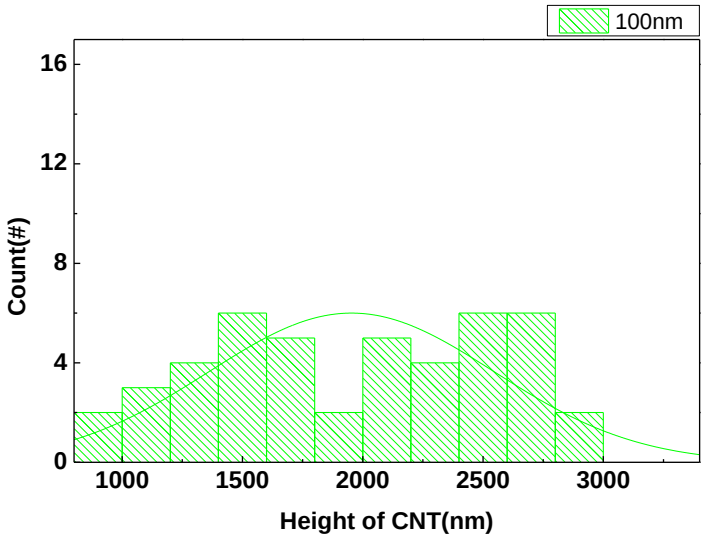


(b)

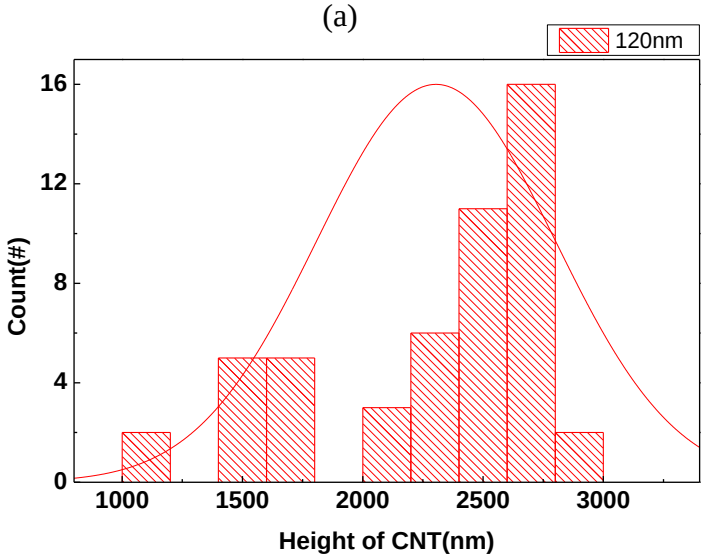


(c)

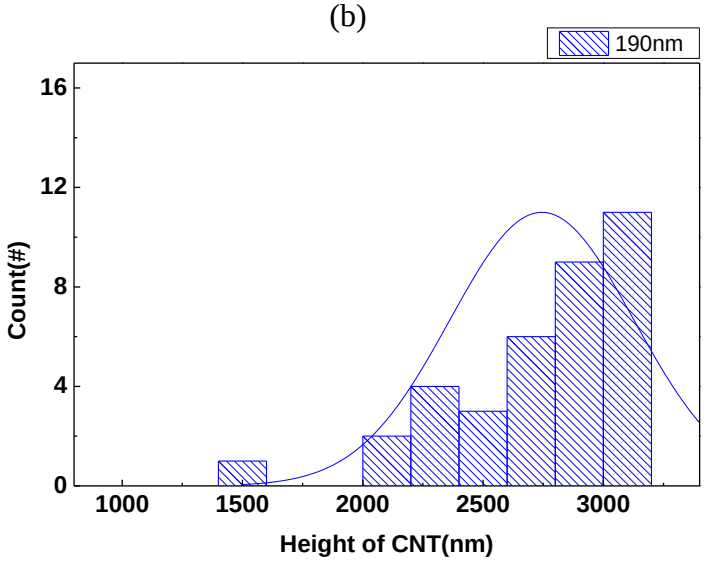
Figure 3.4.3 Histogram data of CNT at 700℃. Catalyst diameters are 100nm(a), 140nm(b), and 180nm(c).



(a)



(b)



(c)

Figure 3.4.4 Histogram data of CNT at 750℃. Catalyst diameters are 100nm(a), 120nm(b), and 190nm(c).

3.5 Multi height CNT array

Fig. 3.7.1 shows the multi height CNT array made by selective CNT growth. The pitch of this array is 1μm and the CNT height is about from 2μm. The catalyst size is from 110nm, 100nm, 90nm, 80nm, and 70nm. 65sccm acetylene gas flow and 650℃ growth parameters were used. We will expect this CNT antenna array's operating frequency from 50 to 130THz calculating from a simple antenna formula applying monopole antenna concept from the principle: $f=C/\lambda$ and $\lambda=L/4$. The expected coverage frequency using this various height CNT antenna array is from 50 to 130 THz. In addition, this antenna can cover every frequency of THz because the frequency can be controlled by the length depending CNT growth time.

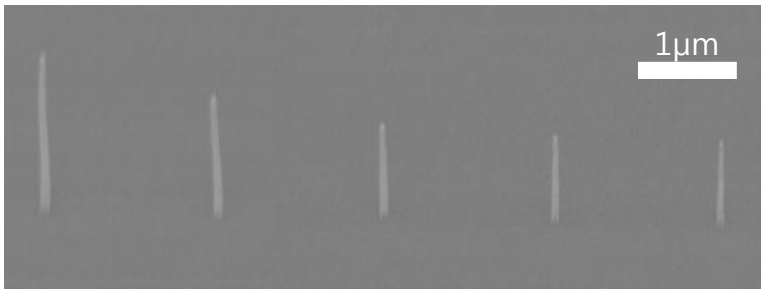


Figure 3.5.1 SEM image of various height CNT array.

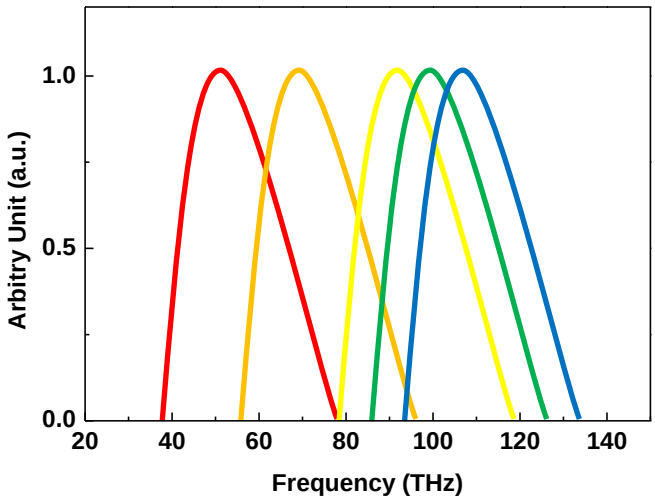
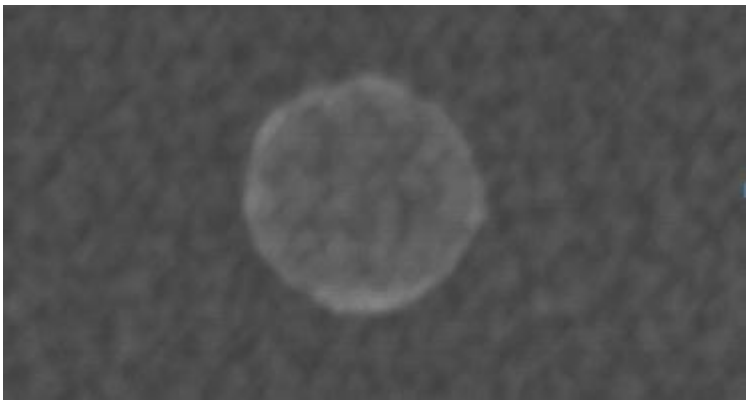


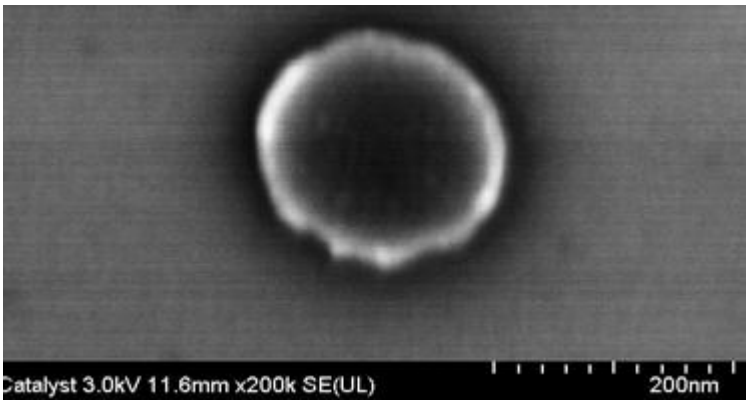
Figure 3.5.2 The calculating operating frequency.

3.6 Si_SiO2_Ni CNT growth

Thin SiO2 layer was tested instead of Nb layer for the improvement of yield ratio because of the layer is smoother than NB layer as shown in figure 3.8.1. Due to the thin SiO2 layer, it does not affect to the condition of e-beam lithography. A different point of design is the 10 Cm pitch in the 10 × 10 array due to the CNT length is longer than CNT growth on Nb layer. The CNT from the catalyst below 100nm does not appear to the graph. It is hard to distinguish the CNT growth based on the catalyst due to short CNT height. The CNT Height is two time long from the morphology different comparing with CNT growth from catalyst on NB. Every data appear small deviation among the CNT growth from different catalyst size when analysis the height result. CNT growth of catalyst on SiO_2 layer shows well aligned CNT in figure 3.8.3. In figure 3.8.4, every data for CNT height shows decrement with decreasing catalyst diameter from 200nm. The yield rate of CNT at every temperature is improved compared with Nb result. Especially, 700℃ and 750℃ increased yield about 20%. Figure 3.8.5 displays the various height CNT array. The CNT position is not matched the position of catalyst. When the nucleation state of catalyst, it is moving due to the flat layer and isotropic structure of nucleation.



(a)



(b)

Figure 3.6.1 The roughness of (a) Nb and (b) SiO_2.

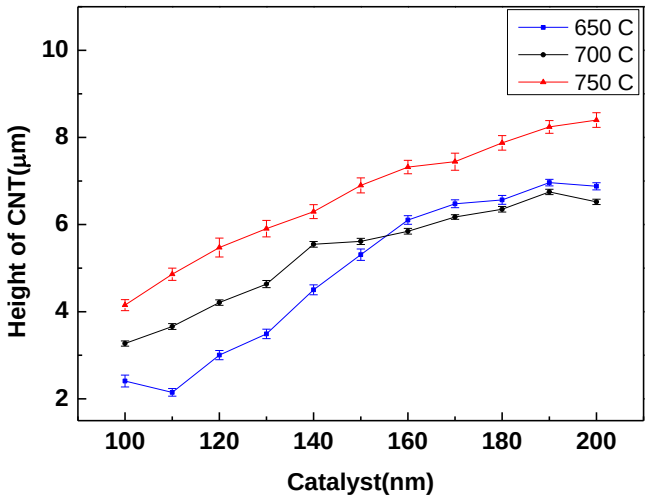


Figure 3.6.2 Height of CNT for each temperature.

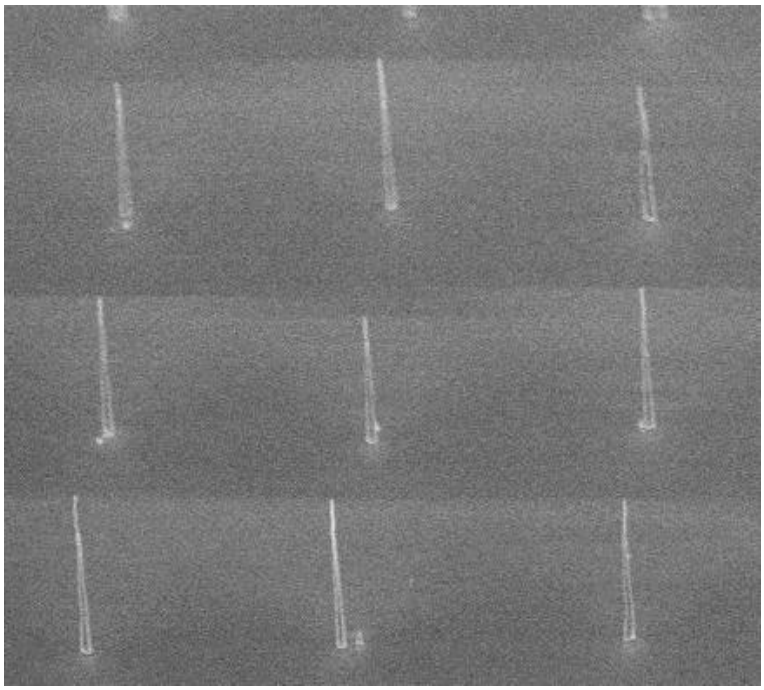
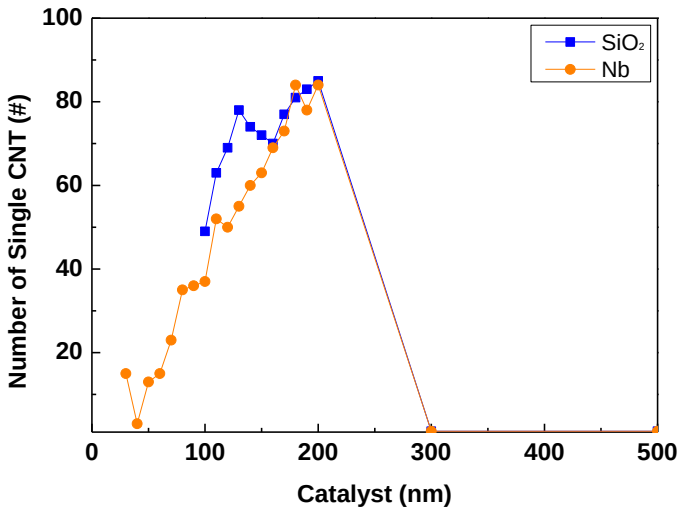
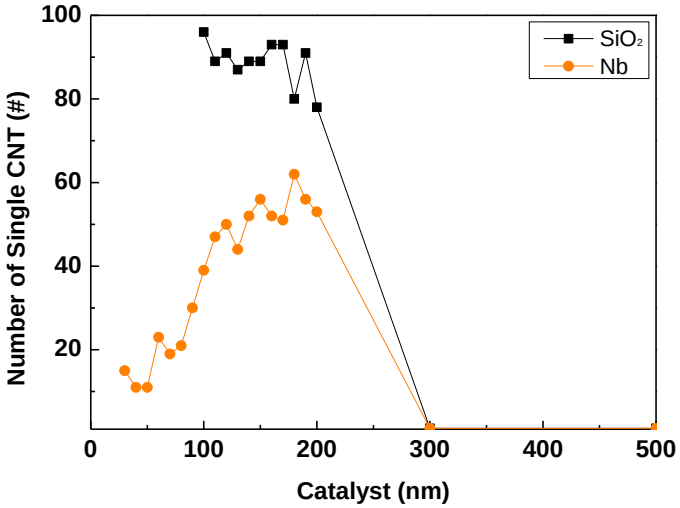


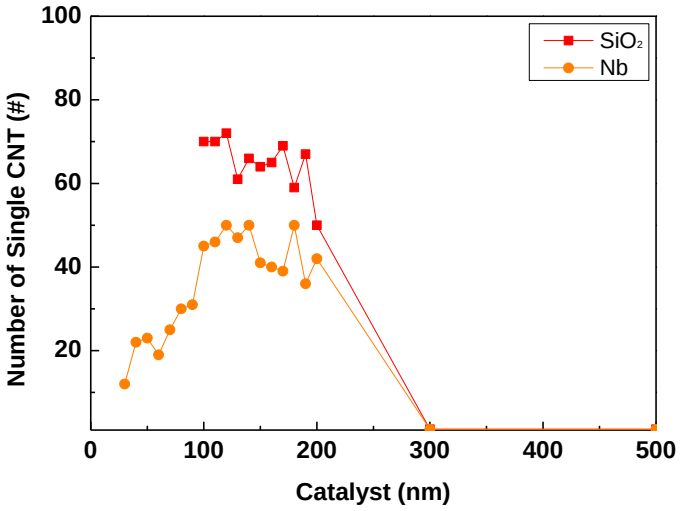
Figure 3.6.3 3×3 single CNT array from 200nm catalyst.



(a)



(b)



(c)

Figure 3.6.4 Counting of single Carbon Nanotube for each temperature.

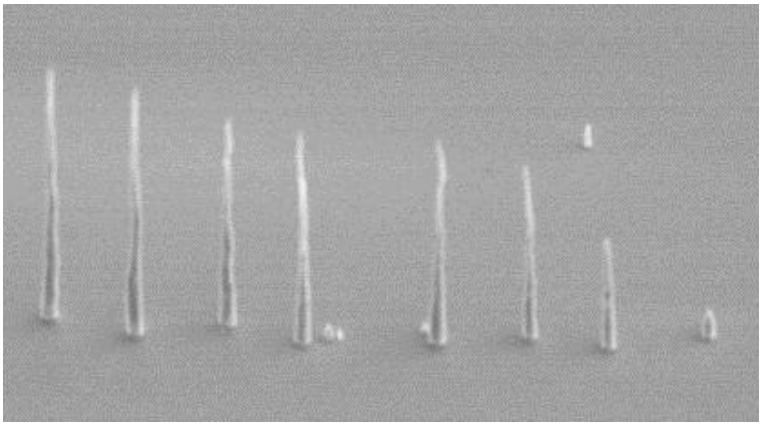


Figure 3.6.5 Various height single CNT array.

Ⅳ. Conclusion

We studied for the nano-optical antenna array structure using vertically aligned single MWCNTs. The e-beam lithography formed the nanometer level catalysts with various sizes on a selective position. Positive resist, PMMA A3, was chosen from the result of the dose test. On the Mo and Nb layer coated substrate, the dose conditions from 300 μ C/cm^2 to 800 μ C/cm^2 can match the size between the design and the result value. We got a good vertical aligned CNT using PECVD with several growth parameters such as plasma bias, catalyst thickness, process temperature, and gas ratio. The CNT growth by AC plasma state showed some serpentine growth caused by the change of the plasma bias. The DC plasma 600V was chosen to solve the problem with minimization of arcing. The proper catalyst thickness is from 10nm to 20nm and the optimum process temperature is 650℃ with ramping up 50℃ /min. 1:4 gas ratio (C_2H_2: NH_3) shows stable vertical CNT growth result. A single CNT growth appeared below the 300nm catalyst diameter. Particularly, the catalyst between 180nm and 200nm showed the highest yield rate on the single CNT growth. Above 300nm, the number of the CNT is more than two due to the formation of two or more nucleation sites during the process of heating the temperature. At the small catalyst, no CNT was grown by the oxidation or the evaporation of catalyst. The heights of the CNT were controlled by the catalyst size. For 10min growth condition, we had CNTs of which the height is 70nm ~11nm. The expected operating frequency is 50 THz to 130 THz as mono-pole antenna concept. Additionally, the length variation at 650℃ was smaller among all other conditions. The single CNT yield ratio also improved the CNT growth on the SiO_2 layer due to the flatness of the layer.

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요 약 문

나노디바이스를 위한 나노광학 안테나 배열 구조

테라 헤르츠 레벨에서 전자기파 신호를 전기적 신호로 바꿔 줄 나노 안테나는 테라 헤르츠 통신이나 광전자공학에서 흥미로운 주제로 연구되어오고 있다. 전통적인 안테나 이론에서는 안테나의 길이는 파장과 깊은 관련이 있다. 특히 빛의 속도, 주파수, 파장의 함수로 된 공식은 테라 헤르츠 통신이 부분적으로 적용이 된다. 그러므로 마이크로에서 나노 단위까지 다양한 다른 길이를 가진 안테나 구조는 매우 높은 주파수에서 다양한 공진 주파수들을 가질 것이다. 그러나 나노 구조체의 높은 저항이나 탑다운 방식의 복잡한 공정프로세스는 테라 헤르츠 영역의 응용에 심각한 문제를 유발한다. 이 논문의 목적은 특정 위치에 다양한 길이를 갖는 탄소나노튜브를 성장 시키는 것이다. 특정 위치에 하나의 다중벽 탄소나노튜브를 성장 시키기 위해서 전자 빔으로 패턴 된 니켈과 PECVD 프로세스가 사용된다. 우리는 촉매의 크기, 아세틸렌 비율, 그리고 온도를 조절한 다양한 탄소나노튜브 길이 대형을 연구하였다. 길이가 300㎚ 이하인 촉매를 사용하여 하나의 탄소나노튜브는 성장시켰다. 온도가 650 인 공정에서 탄소나노튜브의 길이는 짧았고, 하나의 탄소나노튜브 성장이 높은 확률로 나타났다. 탄소나노튜브의 길이는 촉매의 사이즈와 비례 관계로 나타났다. 아세틸렌 가스 양을 늘렸을 때 탄소나노튜브의 길이는 길어졌고 두께는 두꺼워졌다. 우리는 다양한 크기의 나노 안테나를 얻기 위해서 전자 빔 공정을 이용한 다양한 크기의 촉매를 선택했다. 최종적으로 우리는 촉매의 크기를 제어하여서 다양한 길이의 탄소나노튜브를 얻었다.

핵심어: 탄소나노튜브 성장, 나노 안테나, 광학안테나, 나노구조체

감사의 글

작년 2 월에 군대에 입대하는 기분으로 온 산골 깊숙한 곳에 위치한 학교 왔습니다. 건물은 신식인데 책상이랑 컴퓨터조차도 없어서 직접 설치한 지도 어느덧 2 년이 지나서 석사학위를 받게 되니, 시간이 참 빨리 흐른 것 같습니다. 2 년간 석사생활을 해오면서 많은 분들에게 도움을 받아서 이렇게 감사의 글을 적어봅니다. 우선 석사학위 2 년간 든든한 버팀목이 되어주시고, 힘들 때는 격려해주시고 연구가 잘못된 방향으로 갈대 옳은 길로 지도해주신 지도교수님 장재은 교수님께 정말 감사합니다. 지도교수님과 함께 논문은 공동 지도해주신 최홍수 교수님, 최지웅 교수님, 학과에 계신 권욱현 교수님, 손상혁교수님, 김민수 교수님, 박태준 교수님, 은용순 교수님, 박경준 교수님, 정원삼 교수님 감사합니다.

석사생활 동안 함께 같은 랩에서 생활한 후배님들과 그리고 대구경북과학기술원 정보통신융합전공 1 회 석사과정 동기님들 및 2 회 후배님들에게도 감사합니다. 랩실에서 2 년간 함께 고생한 동기 신정희님, 저와 같이 CNT 를 연구하고 저를 많이 도와준 CNT 팀 김승욱 후배님, 자기장 통신을 연구하고 어디로 튈지 모르는 강종구 후배님, 피에조 나노 와이어에 대한 연구하고 개성 넘치는 정예리 후배님, 힘든 석사생활 어려움을 서로 함께 나눈 절친이고 알고 보니 같은 고향인 최인호, 착하고 영어에 대해서 많은 도움을 준 시온, 새침하지만 알고 보면 괜찮은 효찬이, 의젓하고 한결같은 의혁이, 완전 사나이 윤종환 형, 정신적 지주 신상식 형, 아는 게 많으신 류성근 박사님, 초딩 입맛을 가진 성화, 취미가 비슷한 진욱, 재미있는 호경이, 상 받은 호민이, 서울여자 혜린이, 톡톡 튀는 솔이 외에도 후배님들 감사합니다.

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