Controlled Fabrication and Assembly of Carbon Nanotubes based Nanostructures

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Abstract

This project focuses on the controlled methods of fabrication and assembly of carbon nanotube based nanostructures as future nanoscale building blocks. Large scale (on 4-inch wafer) vertically aligned multi-walled carbon nanotubes array on Ti electrodes with controlled position as potential vertical interconnect or biosensing probe is fabricated by plasma-enhanced chemical vapor deposition. Spin-on glass is found to be good candidature for insulating layer coating on this structure. The total resistance of the CNT-Ti electrode structure is measured to be 10 kΩ on average. Individual carbon nanotube is also deposited on SiO₂ surface with controlled position and direction by modifying the SiO₂ surface with APTS patterned PMMA trench. The width of PMMA trench needs to be smaller than 1 μm to have single CNT deposited. Carbon nanotubes are also placed between electrodes with controlled position and direction by dielectrophorectic force. Centrifugation of CNTs solution is found to be effective to reduce the number of junk particles. With proper electrode configuration and CNT solution concentration, individual CNT can be precisely positioned between electrodes. Comparisons between electric field simulation and experiment results show that CNTs are driven to the higher field density region by dielectrophorectic force and aligned along the electric field direction. By manipulating the electrodes geometry, electric field could be modified in the intensity and direction. This paves the way for using ac dielectrophoresis to align nanostructures in complex circuits.
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Chapter One – Introduction

For nanostructured materials (e.g. nanotubes, nanowires and nanoparticles), the presence of small volumes, free surfaces and strong bonding can dramatically alter mechanical and electrical behavior. Because of unique bonding configurations and quantum mechanical size effects, coupling between mechanical and electronic properties can be observed in many of these systems.

Figure 1.1 shows the density of electron states as the dimensionality of the structure decreases. Electron transport property of a nanostructure is very different from the bulk material. For example, in the case of one dimension material, carbon nanotube (CNT), at low temperature, charge transport in CNT is ballistic in the micrometer range if no defects are present due to the translational symmetry of the tube along the axis. The resistance of the tube is virtually independent of the length at the scale of interest. The absence of scattering along the tube allows current densities of more than 1000 times that in polycrystalline metals [1, 2]. The electron transport properties of the carbon nanotube connected to metallic electrodes depends on the carbon nanotube-metal junction, and may change with increasing transparencies of the junctions: from the Coulomb blockade regime, through the Kondo effect, and Fabry-Perot resonator-like behavior up to the Fano resonance.[3]
1.1 General Characteristics of Carbon Nanotubes

Carbon nanotubes were discovered by Sumio Iijima in 1991. Since then, they have been of great interest among the scientific community as well as the engineering community, both from a fundamental science point of view and for future applications. Their large length (up to several microns) and small diameter (several nanometers) result in a large aspect ratio. Therefore, carbon nanotubes are expected to possess extraordinary electrical, mechanical and chemical properties.
There are two types of carbon nanotubes: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs), which are shown in Figure 1.2. Single-walled nanotubes have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. The structure of a SWCNT can be imagined by wrapping a one-atom-thick layer of graphite, called graphene, into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices \((n,m)\) called the chiral vector (figure 1.3).
The integers \( n \) and \( m \) denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If \( m=0 \), the nanotubes are called "zigzag" (figure 1.4 (a)). If \( n=m \), the nanotubes are called "armchair" (figure 1.4 (b)).

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a \((n,m)\) nanotube, if \( n-m \) is a multiple of 3, the nanotube is metallic, otherwise the nanotube is semiconducting. So all armchair \((n=m)\) nanotubes are metallic [4].

MWCNTs have more than one shell with increasing diameters from innermost shell to the outmost shell. The diameter of the outmost shell typically ranges from 10 nm to 100 nm.
Carbon nanotubes are also exceedingly strong mechanically, chemically and thermally very stable and have excellent thermal conductivity. These unique properties of carbon nanotubes make them the object of extensive studies in both basic science and technology. A great challenge for nanotubes is the ability for controlled fabrication of semiconducting or metallic CNTs, as well as the difficulties in manipulating individual carbon nanotube in a controlled way.

1.2 Potential Application of Carbon Nanotubes

Carbon nanotubes have attracted much attention around the world with their unique properties, which may lead to lots of promising applications. Potential practical applications have been reported such as electronic devices [5], nanoelectronic devices [6], high sensitivity nanobalance for nanoscopic particles [5], supercapacitors [7], field emission materials [8], nanotweezers [9], hydrogen storage [10] and chemical sensors [11]. New applications are likely in the diamond industry since experiments have shown the conversion of carbon nanotubes to diamond under high pressure and high temperatures with the presence of a certain catalyst [12]. Carbon nanotube is also a candidate to use as interconnects or FET channels in electronics devices when the current silicon technology reaches its fundamental size limit [13]. Figure 1.5 shows a model of Infineon's 18nm nanotube transistor [14]. These are just a few possibilities
that are currently being explored. As more research and development are conducted, the potential applications of CNTs will continue to increase.

Figure 1.5 Model of Infineon’s 18nm nanotube transistor[14]
1.3 Motivation for the project

As shown in the previous section, carbon nanotubes indeed have many fascinating properties as nanoscale building blocks. However, their use in practical devices still has great challenges. One critical challenge is to develop a technology that enables precise placement of individual carbon nanotube on the substrate. For practical applications, carbon nanotube must be positioned on exact substrate locations, so it could be electrically addressed and connected to the macroscopic outside world. The lack of a solution for the controlled deposition of carbon nanotubes at given locations on the wafer is a major bottleneck. Although a great deal of work has been carried out to look for a possible solution, how to place the nanotubes at desired locations with targeted shapes, directions, and densities for fabricating functional devices are still unsolved problems. As silicon devices approach fundamental scaling limits, methods are urgently needed to assemble carbon nanotubes over large-scale areas with controllable morphology, location, orientation, and density. All these promising properties of carbon nanotubes, potential applications and the difficulties in the controlled fabrication and assembly motivate the author to explore large-scale fabrication of carbon nanotube based structures with controlled parameters and assembly of carbon nanotubes with single tube precision in this project.
1.4 Objectives of the project

Methods of controlled fabrication and assembly of carbon nanotube based structures such as interconnects, probes and FET channels will be explored. Wafers with large-scale vertically-aligned CNT array in contact with metal electrodes will be fabricated with controlled tube position. Single CNT is going to be placed horizontally on the wafer surface with controlled position by patterned deposition. Individual carbon nanotube is going to be positioned between electrodes by dielectrophoresis with controlled position. There are three main objectives in this project:

- To fabricate large-scale vertically aligned carbon nanotubes array on metal electrodes with controlled position and test the basic electrical property of the structure.

- To control the positioning of carbon nanotube in a horizontal direction on a wafer surface by patterned deposition. Based on the experiment results, to suggest the optimum patterning parameters for depositing single nanotube with controlled position.

- To control the positioning of carbon nanotube between metal electrodes with single tube precision by dielectrophoresis and analyze correlation between carbon nanotube positioning and electric field intensity.
1.5 Scope of Thesis

This thesis is divided into 7 chapters. Chapter 2 presents a literature review of the topic of carbon nanotube properties, fabrication and methods to achieve controlled positioning. Chapter 3 focuses on the fabrication of carbon nanotubes using chemical vapor deposition (CVD) process. Aspects of experiment process and the parameters studied will be discussed. Chapter 4 shows the fabrication process of large-scale carbon nanotube based microelectrode-array structure, which has potential applications as probes, interconnects, vertical channels and so on. Basic electrical property of the structure will be shown. Chapter 5 explores the precise carbon nanotube deposition on silicon dioxide by chemically modifying the wafer surface. Chapter 6 focuses on the positioning of carbon nanotube between electrodes by dielectrophoresis. The effects of process parameters such as concentration of carbon nanotube suspension, electric field intensity and direction will be discussed. The method of precisely positioning a single tube between electrodes will be presented. Basic electrical property of single carbon nanotube will be shown. Lastly, the report will be concluded in Chapter 7.
Chapter Two – Literature Review

2.1 Background

In 1959, Professor Richard Feynman gave a seminal talk at the annual meeting of the American Physical Society at the California Institute of Technology, in which he first envisioned the impact of things at ultra-small scale on future science and technology. The topics that have been covered by his talk include but are not limited to data storage, electron microscope, biology, small machine, manipulation of atoms and so on. Great progress has been made after 1959. Nanostructures became a broad and interdisciplinary area of research and development activity. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed.

Silicon-based microelectronic devices have revolutionized the world in the past three decades. Integrated circuits, built up from many silicon devices (such as transistors and diodes) on a single chip, control everything from cars to cell phones, not to mention the Internet. The desire for cheaper electronic memory, and faster processors, is still not satisfied. Every year, more powerful chips with smaller device size are introduced. The miniaturization of the devices found in integrated circuits is predicted
by the semiconductor industry roadmap to reach atomic dimensions in 2012. According to Muller, silicon devices will then reach their fundamental physical limit. [15]

![Figure 2.1 Top down and Bottom up approach](image)

As the top-down approach is reaching its limit, researchers are intensively developing the bottom-up processes. Various kinds of nanoparticles [16], nanowires [17] and nanotubes are used as building blocks for next generation electronic devices. There has been intense effort to develop carbon nanotubes for electron transport in the next generation of devices. The small diameter of single-walled carbon nanotubes (SWCNTs), along with their long length, low scattering, and almost ballistic transport, makes them very attractive as potential channels in field effect transistors (FETs). Figure 2.2 shows the model of Infineon’s vertical carbon nanotube transistor [18]. Great effort has been expended to integrate these
FETs into logic gates and logic circuits [19].

Figure 2.2 Model of Infineon’s vertical carbon nanotube transistor [18]

Great challenges still need to be overcome for nanotubes to be viable as channels and interconnects in FETs. Among these, the precise positioning of nanotubes in devices needs to be addressed.

Several methods have been proposed to achieve controlled positioning of carbon nanotubes, including chemical modification of the substrate [20], growing nanotubes on a substrate directly by chemical vapor deposition [21], the mechanical transfer protocol [22], and the use of dielectrophoresis to position carbon nanotubes in electrode gaps [23-25]. All the methods could be divided into two groups: positioning by direct growth and post-synthesis positioning.
2.2 Growth of carbon nanotubes

The techniques for production of carbon nanotubes can be roughly divided into three main classes: Arc-discharge, Laser ablation and Chemical vapor deposition.

2.2.1 Arc-discharge

In the arc-discharge technique (figure 2.3), an electric arc is generated between two graphite electrodes under a helium or argon atmosphere, which causes the graphite to vaporize and condense on the cathode. The deposit contains the nanotubes and also fullerenes, amorphous carbon materials and catalyst particles. This technique requires further purification to separate the CNTs from the by-products. The electrodes of graphite are doped with catalytic metal atoms (Ni, Co) for the production of SWCNTs.

Figure 2.3 Diagram illustration of the arc-discharge technique (Thostenson et al 2001).
2.2.2 Laser Ablation

The laser ablation method is the second technique for producing carbon nanotubes (figure 2.4). This process is known to produce CNTs with the highest quality and high purity of single walls [26]. In this process, a piece of graphite is vaporized by laser irradiation under an inert atmosphere. With every laser pulse, a plume of carbon and metal vapors emanates from the surface of the target, and CNTs start to grow in the gas phase. This results in soot containing nanotubes. They are then collected on a water-cooled target. Two kinds of products are possible: multi-walled carbon nanotubes or single-walled carbon nanotubes. The graphite target is doped with cobalt and nickel catalyst to produce single-walled nanotubes [27]. For this process, a purification step by gasification is also needed to eliminate carbonaceous material.

Figure 2.4 Schematic illustration of the laser vaporization technique (Guo et al 1995).
2.2.3 Chemical Vapor Deposition

In the chemical vapor deposition (CVD) process growth involves heating a catalyst material to high temperatures (500-1000 °C) in a gaseous hydrocarbon precursor over a period of time. The basic mechanism in this process is the dissociation of hydrocarbon molecules catalyzed by the transition metal and saturation of carbon atoms in the metal nanoparticle. Precipitation of carbon from the metal particle leads to the formation of tubular carbon solids in a sp² structure [28]. The characteristics of the carbon nanotubes produced by the CVD method depend on the working conditions such as the temperature and the pressure of operation, the volume and concentration of source gas, the size and the pretreatment of metallic catalyst, and the time of reaction. The type of carbon nanotube produced depends on the metal catalyst used during the gas phase delivery. In the CVD process, single-walled nanotubes are found to be produced at higher temperatures with a well-dispersed and supported metal catalyst while multi-walled nanotubes are formed at lower temperatures [29]. Purification is needed to eliminate impurities formed during the process such as graphite compounds, amorphous carbon, and metal nanoparticles. This is achieved by oxidative treatments in the gaseous phase, liquid phase, acid treatment, microfiltration, thermal treatment and ultrasound methods.
Chapter 2 – Literature Review

2.3 Positioning of carbon nanotubes

Carbon nanotubes have many fascinating nanoscale properties and they are believed to be the most promising nanoscale building blocks. However, for practical applications, the building blocks must be positioned on exact substrate locations to be electrically addressed and connected to the macroscopic outside world. How to place the nanotubes at desired locations with targeted shapes, directions, and densities for fabricating functional devices has been one of the longstanding unsolved problems. Much effort in two areas, which may be classified into direct-growth and post-synthetic approaches, has been made to address this issue.

2.3.1 Field guided growth

Figure 2.5 SEM images showing electric field directed SWCNTs growth (a) E=0V/µm, (b) DC bias, E=0.5V/µm [30]
The electric field was exploited to guide the growth of carbon nanotubes. Dai and co-workers have demonstrated the effectiveness of electric fields in the growth of SWCNTs (Figure 2.5) [30]. During the growth of SWCNTs in the chemical vapor deposition chamber, the external electric fields were applied across the predefined trenches and the SWCNTs were grown along the electric fields due to their high polarizability. These examples indicate that the electric-field assisted assembly is a viable strategy bearing a potential to be exploited for the fabrication of functional devices.

Vertically-aligned carbon nanotubes could be grown by plasma-enhanced chemical-vapor deposition (PECVD). Electric field in the sheath region of plasma is used to guide the growth direction of carbon nanotubes. The growth direction is usually parallel to the electric field direction. PECVD is similar to thermal CVD, which also uses gaseous sources. The difference is that in thermal CVD heat is used to activate the gas, whereas in PECVD the molecules are activated by electron impact. In the simplest case of a dc plasma reactor, a dc voltage is applied across a space filled with a low-pressure gas. The glow discharge that is initiated can be divided into three visible regions arranged from cathode to anode: (1) cathode dark space, (2) negative glow, and (3) Faraday dark space. The dc discharge is maintained by the processes at the cathode and in the dark space. The ions are accelerated by the applied voltage and some of them bombard the cathode. This impact generates secondary electrons
that accelerate away from the cathode. The collisions excite molecules and energetic electrons ionize some of them. The negative glow is the result of this excitation process. The thickness of the dark space is related to the electron mean free path. [31] The current in the dark space is carried primarily by ions, while in the negative glow it is carried by electrons. Thus, the negative glow is a low impedance region and the applied voltage drops mostly over the dark space. The dark space varies from a few hundred micrometers to a few millimeters. Application of several hundred volts can create electric fields on the order of $10^4$ V/cm.

Figure 2.6 Schematic representation of the PECVD process for growing vertically aligned carbon nanotubes. (a) Catalyst deposition, (b) catalyst pretreatment/nanoparticle formation, and (c) growth of carbon nanotubes[32]
Chapter 2 – Literature Review

Figure 2.6 shows a schematic diagram of the PECVD process. PECVD using dc plasma also possesses some limitations. For example, the power delivered into the plasma and the substrate bias is inextricably coupled, which limits the process control. Plasma instability is also a drawback of a dc discharge. [33] Alternatively, a radio frequency (RF) plasma system, in which the polarity of the electrodes changes fast enough to avoid surface charging, can be used.

(a)                                 (b)

Figure 2.7(a) shows MWCNFs at a bias voltage of $-550\text{V} (360\text{W}, 670\text{ mA})$ (b) Increasing the bias to $-600\text{V} (470\text{W}, 780\text{ mA})$ gives exclusive growth of MWCNTs. [34]

The plasma power, dc voltage bias and current are important parameters for a PECVD process. Delzeit and his coworkers showed that higher CVD power and dc bias reduced the diameter of carbon nanotubes [34]. They grew CNT from patterned 20 nm thick nickel catalyst film on a
100 nm thick chromium underlayer. When the power and dc bias is 360W and -550V, mainly carbon nanofibers, which have a larger diameter than nanotubes, were grown (figure 2.7(a)). When the power and dc bias are increased to 470W and -600V, only multi-walled carbon nanotubes were seen (figure 2.7(b)).

![Figure 2.8 Growth of nanotubes on lithographically defined areas [35]](image)

In a PECVD process, the growth location of the vertically-aligned carbon nanotubes could be controlled by the patterned deposition of the catalyst layer. Figure 2.8 shows an impressive demonstration of nanotubes growth on selected areas, growth of nanotube on lithographically defined areas [35].
2.3.2 Patterned deposition

Motorola has reported on the high density selective placement of carbon nanotubes horizontally by patterned position (figure 2.9). They first patterned trenches in PMMA on SiO₂ substrates using electron beam lithography. They treated SiO₂ with aminopropyltriethoxysilane (APTS) vapor. Carbon nanotubes solution was made using N-methyl pyrolidone (NMP) as a solvent, and the solution was centrifuged for 10 min at speeds up to 28000 rpm to remove junk particles. Finally, carbon nanotubes have been dispersed on an APTS treated SiO₂ surface. In this way, they could control the positioning of carbon nanotubes. They claimed the selectivity was very high, as no nanotubes were adhered on non-silanised SiO₂. Carbon nanotubes in narrow stripes were found to be better aligned than in larger stripes [36].
2.3.3 Dielectrophoresis

Dielectrophoresis has been studied to position carbon nanotubes in electrode gaps, which leads to much better control of alignment [23-25]. In 2006, Herman and his coworkers from Columbia University reported controlled placement of SWCNTs in four-electrode geometries (figure 2.10), by using floating metal posts to perturb the electric field locally and controllably [37]. They claimed the approach could enable the desired placement of SWCNTs in multi-electrode structures.

Figure 2.10 (a) SEM micrographs showing carbon nanotubes dielectrophoretically aligned along adjacent electrodes (b) Dielectrophoretically aligned tubes as in (a) but with two 300 nm diameter posts near the center of the 3 μm gap. White arrows are used to point out the two metal posts in the gap, one of which is bright and the other is dark.
In 2006, Krupke and his coworkers developed a bulk-separation method dielectrophoresis [38]. They produced thin films of only metallic SWCNTs between electrodes (figure 2.11). The claimed that dielectrophoretic separation of metallic from semiconducting tubes on the basis of their different dielectric properties has advanced in processing larger nanotube quantities without sacrificing the intrinsic high selectivity of the process—a development that is promising for the development of nanotube-based electronic-device applications.
Chapter Three – Fabrication of Carbon Nanotubes by CVD process

3.1 Objective

The objective of the whole project is to explore controlled fabrication and assembly of carbon nanotube-based nanostructures. It is necessary to explore the growth methods of carbon nanotubes. Direct growth is one of methods to control the positions of carbon nanotubes. Among all the direct growth techniques, the chemical vapor deposition (CVD) method is especially attractive because it can be easily scaled to mass production and is ideally suited to growing nanotubes for advanced applications in the fields of electronics. Thermal CVD and plasma-enhanced CVD are the two main CVD methods for both single-walled and multi-walled carbon nanotube growth. Plasma enhanced CVD (PECVD) is able to control the alignment and orientation of carbon nanotubes [39]. As a preparation for realizing the controlled positioning of carbon nanotubes by CVD direct growth, multi-walled carbon nanotubes growth by both thermal CVD and PECVD is to be explored in this chapter.
3.2 Methodology

In the experiments, multi-walled carbon nanotubes were firstly grown by the CVD process, and vertically aligned multi-walled carbon nanotubes were then grown by the PECVD process. The main procedures for the two processes are similar; the differences being the parameter of the catalyst thickness and the CVD conditions.

Figure 3.1 shows a process flow of growth process. The test die was firstly cleaned, and then it was coated with the catalyst layer, finally it went through the high temperature CVD process.

Figure 3.1 Procedures for Growth of Carbon Nanotubes
3.2.1 Cleaning procedure of test die

In all the experiments, test dies were cleaned with standard cleaning procedures before use. They were immersed in acetone and cleaned by an ultrasonic machine for 10 minutes, and then immersed in isopropyl alcohol (IPA) and put into the ultrasonic cleaning machine for 10 minutes. Test dies were then dried in a nitrogen stream.

3.2.2 Catalyst Coating

Transition metals such as iron, cobalt and nickel were found to be catalysts for the growth of carbon nanotubes [40]. In order to obtain nanotubes, the catalyst has to be made into a thin layer.

There are various methods to coat a catalyst layer on the die surface, including Sol-gel method [40], Ion-adsorption-precipitation [41], physical deposition, and so on. The catalyst coating in this project uses physical deposition. Catalyst material is directly evaporated onto the test die surface.

After cleaning, test dies were coated with a catalyst material by a thermal evaporation (figure 3.3). There are standard procedures for coating. The working principle of evaporator is shown in Figure 3.2.
Chapter 3 – Fabrication of Carbon Nanotubes by CVD process

The chamber of the evaporator is kept in vacuum. Catalyst sources are placed on an electrical heater. The heater power could be controlled by adjusting the current value. When the temperature of the heater reaches the melting point of the catalyst material, the catalysts melt gradually, and then are vaporized. The catalyst vapor falls on the surface of the test die, which is placed just above the heater, and then the vapor freeze to solid state again. A thin layer of catalyst material is formed on the sample surface.
Chapter 3 – Fabrication of Carbon Nanotubes by CVD process

There is a detector which shows the thickness of the catalyst layer coated, having a resolution of 0.1 nm. Nickel is coated as catalyst material in this project.

3.2.3 Catalyst annealing

There is a consensus in the literature on the correlation between the size of the catalyst nanoparticles and the carbon nanotube diameter [49-56]. The relevant size of the nanoparticles for the resulting diameter of the CNTs is their size at the time of nucleation. The morphology of catalyst also determines the type of the growth CNTs, tip-growth or base-growth (figure 3.4).
Figure 3.4 Tip-growth and Base growth of Carbon nanotubes[48]

Before the CVD process, the die with the catalyst layer is annealed at 700 to 800 °C. Upon annealing, the equilibrium shape of the catalyst may be reached. There are two types of possible shapes, which depend on the interface between catalyst material and the underlayer (figure 3.5). The Young’s equation describing a contact between two phases A and B is considered.

\[ \gamma_A = \gamma_{AB} + \gamma_B \cdot \cos \theta \]

with \( \gamma \) the corresponding interface energies, \( \theta \) the angle between the die surface and catalyst interface surface.
Figure 3.5 Conditions on the surface energies of substrate (A), deposit (B) and interface A-B in determining the type of growth: (a) tip-growth or (b) base-growth.

The size of the catalyst particles after annealing directly depends on the thickness of the deposited material [42-45]. For breaking up the thin film obtained after deposition, some literature reported the use of NH₃ [46] during annealing to change surface energies $\gamma_A$ and $\gamma_B$. The shape of the catalyst particle after annealing will determine the type of growth CNTs: tip-growth or base-growth [47].

### 3.2.4 Chemical Vapor Deposition

After annealing, thermal CVD or PECVD process is used to grow multi-walled carbon nanotubes in this project. Both methods use the same experiment set up. A schematic of the CVD system is shown in Figure 3.6.
Chapter 3 – Fabrication of Carbon Nanotubes by CVD process

Figure 3.6 Schematic of Chemical Vapor Deposition System

The parameters for growth of carbon nanotubes using CVD system include the following:

- Flow rate of NH$_3$ (sccm-Standard Cubic Centimeters per Minute, Where "Standard" means referenced to 0 degrees Celsius and 760 Torr)
- Flow rate of C$_2$H$_2$ (sccm)
- Temperature of the heater
- Plasma voltage and current
- Pressure
- Growth duration
The CVD process for growth of carbon nanotubes is as follows:

- The test die was firstly placed on the heating element and the chamber was pumped down by opening rough pumping valve, and the main gas valve.
- The NH$_3$ and C$_2$H$_2$ flow rate were preset through the controller. Once the chamber pressure reached the base level, the NH$_3$ gas valve was opened to fill the chamber with NH$_3$. Rough pumping valve was closed and the fine pumping valve was used to control the pressure to the required level.
- Heat up the element to the required temperature, by using the pyrometer to check. Anneal the test die for the required duration.
- If it is thermal CVD, the C$_2$H$_2$ valve was opened to release the gas into the chamber after annealing. If it is Plasma-Enhanced CVD, strike the plasma after annealing and immediately opened the C$_2$H$_2$ valve.
- After the required time for growth, the C$_2$H$_2$ valve was closed to stop the gas. The plasma was turned off, and the heater was turned off slowly. NH$_3$ gas valve was finally closed. After some time for the chamber to be cooled down, vent the chamber.

**Plasma Enhanced Chemical Vapor Deposition (PECVD)**

CNTs grown by PECVD are more vertically-aligned than thermal
CVD-grown structures. The carbon nanotubes are submerged inside the sheath where a large electric field exists in the direction normal to the substrate. Merkulov and his coworkers proposed an alignment mechanism depicted in figure 3.7[48]. As growth proceeds, CNTs may bend if there are spatial fluctuations in the carbon precipitation. This would lead to nonuniform stresses at the particle/CNT interface. The electrostatic force $F$ creates a uniform tensile stress across the entire particle/CNT interface, regardless of where the particle is located (tip or base). Further work is still needed to fully explain the alignment observations.

Figure 3.7 Carbon nanotube Alignment mechanism during PECVD as proposed by Merkulov. [48]
3.3 Experiment and Results

3.3.1 Thermal chemical vapor deposition

Thermal CVD was first tried to grow multi-walled carbon nanotubes. The optimum process parameters were found to grow multi-walled carbon nanotubes after several trials. The test die used is a 5 X 5mm² silicon die with 400nm silicon dioxide layer on top. A layer of nickel with 5 nm thickness was coated on the SiO₂ surface as catalyst. The die was annealed at 650°C for 15 minutes with 6 mbar NH₃ environment. The CVD process was carried out immediately after the annealing. The parameters of CVD are listed as below:

- Flow rate of NH₃ is 60 sccm
- Flow rate of C₂H₂ is 6 sccm
- Chamber Pressure is maintained at 7.5 mbar
- Temperature is maintained at 700 °C
- Duration of growth is 5 minutes

Figure 3.8 Multi-walled carbon nanotubes grown by thermal CVD
Figure 3.8 shows the carbon nanotubes observed using a scanning electron microscope (Philip XL30). Clumps of carbon nanotubes on the test die were observed. The length of the tubes is $10\mu m$ on average, and the diameter ranges from 20 to 50 nm. In figure 3.9, the TEM image shows the diameter of the nanotube is around 30 nm. The wall structure is shown in the higher magnification image (figure 3.8 (b)). The number of wall layers is about 30.

![Figure 3.8 TEM images of carbon nanotubes grown by thermal CVD process](image)

(a)                                (b)

Figure 3.9 TEM images of carbon nanotubes grown by thermal CVD process

3.3.2 Plasma-enhanced chemical vapor deposition

In this experiment, vertically aligned carbon nanotubes were grown by plasma enhanced chemical vapor deposition. CNTs growth was attempted
on three types of dies with different surface material, which are SiO$_2$, Si$_3$N$_4$, and Ti surface.

3.3.2.1 Vertically aligned MWCNTs growth on SiO$_2$ surface

5 X 5 mm test dies with Si substrate and 400nm SiO$_2$ surface layer were used. 5nm layer of Ni was evaporated as catalyst on the test die surface. Before CVD, the test die was annealed at 700°C for 5 minutes. The parameters of the PECVD process are as following:

- Flow rate of NH$_3$ is 60 sccm
- Flow rate of C$_2$H$_2$ is 6 sccm
- Pressure is maintained at 7.5 mbar
- Temperature is maintained at 700°C
- Plasma voltage is 560V, current is 48.5 mA
- Duration of growth is 10 minutes

SEM image (figure 3.10) shows the diameter of the carbon nanotubes ranges from 50 to 100 nm. The catalyst is at the end of every tube, which indicates it is tip growth. Tilted SEM image (figure 3.11) shows the shape of the catalyst. Compared with figure 3.5, it could be seen that the growth mechanism is tip-growth.
Figure 3.10 SEM image shows carbon nanotubes grown by PECVD on SiO$_2$

Figure 3.11 30 degree tilted SEM image shows carbon nanotubes (a small portion of the tubes have larger diameter, which could be nanofibers)
3.3.2.2 Vertically-aligned MWCNTs growth on metal surface

5 X 5 mm\(^2\) test dies with Si substrate and Ti electrodes were used to grow carbon nanotubes. This experiment is to test the fabrication conditions of carbon nanotubes growth on metal surface. Ti was used because it could withstand the high temperatures during the PECVD process. Ti was also reported to have good electrical contact property to carbon nanotubes by other research groups [57-60]. 5nm layer of Ni was evaporated as catalyst on the test die surface. Before CVD the test die was annealed at 700\(^\circ\)C for 5 minutes. The parameters of the PECVD process are as follows:

- Flow rate of NH\(_3\) is 60 sccm
- Flow rate of C\(_2\)H\(_2\) is 6 sccm
- Pressure is maintained at 7.5 mbar
- Temperature is maintained at 700 \(^\circ\)C
- Plasma voltage is 520V, current is 52.5 mA
- Duration of growth is 10 minutes
Figure 3.12 SEM image of carbon nanotube grown by PECVD on Ti surface

SEM image (figure 3.12) shows the diameter of the carbon nanotubes ranges from 50 to 100 nm. Catalysts are at the top end of the tubes, which indicates that the growth mechanism of carbon nanotubes is also tip-growth.

3.3.2.3 Vertically-aligned MWCNTs growth on Si$_3$N$_4$ membrane

In this experiment, vertically aligned carbon nanotubes growth has been attempted on Si$_3$N$_4$ membrane. The test die is 3 X 3 mm$^2$, and composed of Si substrate and 150nm Si$_3$N$_4$ membrane window. A square window was patterned at the center of the die from back-side by photolithography. Si was then etched by KOH solution. 100 X 100 μm$^2$ Si$_3$N$_4$ membrane was made at the center of the die in this way. This structure was fabricated to carry out some TEM analysis work on carbon nanotubes. Various shapes
including square, circle and triangle have been cut on the membrane by focused ion beam. The Si$_3$N$_4$ surface was then coated with 5 nm nickel as catalyst for CVD grown of carbon nanotubes. Before CVD, the test die was annealed at 700°C for 5 minutes. The parameters of the PECVD process are as follows:

- Flow rate of NH$_3$ is 60 sccm
- Flow rate of C$_2$H$_2$ is 6 sccm
- Pressure is maintained at 7.5 mbar
- Temperature is maintained at 700 °C
- Plasma voltage is 520V, current is 43 mA
- Duration of growth is 5 minutes

Figure 3.13 SEM image of vertically aligned MWCNT grown on Si$_3$N$_4$ membrane

SEM images (figure 3.13) show vertically aligned carbon nanotubes were grown uniformly on membrane. The length of the carbon nanotubes is
5 μm, and the diameter is about 100 nm on average. The growth mechanism is also tip-growth.

### 3.4 Summary

Carbon nanotube CVD growth process is the decomposition of hydrocarbon with the aid of transition metal catalysts. The property of carbon nanotubes grown are affected by many parameters, such as the thickness of the catalyst layer, the temperature and pressure of the CVD chamber, the gas flow rate and the substrate material. The diameter of the carbon nanotube mainly depends on the size of the catalyst particle. The size of the catalyst particle depends on the thickness of the coating layer, the temperature of the annealing and the substrate material. By properly tuning these parameters, multi-walled carbon nanotubes could be grown with desired diameter and length.

Multi-walled carbon nanotubes grown by thermal CVD usually lie on the die surface with no defined direction. Plasma Enhanced CVD could control the growth direction of carbon nanotubes. Nanotube growth direction follows the electrical field direction of the sheath of the plasma, which is perpendicular to the local surface plane of the test die. So the growth direction of carbon nanotubes could be controlled by modifying the test die surface.

The location and quantity of carbon nanotubes grown could be further
controlled by precisely defining the catalyst location and thickness. The ability to control the position of carbon nanotubes is crucial for producing carbon nanotube-based electronics devices, such as CNTFET and CNT probes. The experiment on large-scale fabrication of carbon nanotubes array with controlled position by CVD growth will be discussed in Chapter Four.
Chapter Four – Fabrication of Carbon Nanotubes based Microelectrode Array

4.1 Objective

The ability to have carbon nanotubes on a substrate at a desired position is a great challenge from a technological point of view. CVD growth could control the position of the carbon nanotubes by defining the position of the catalyst. This control over the CVD growth of CNTs would permit the integration of the carbon nanotubes growth into fabrication processes of microelectronic circuits since the CVD process requires much lower temperatures than the arc-discharge and laser-ablation processes [61]. Several research groups have already experimented on the control of carbon nanotubes growth position and direction by the CVD method [62-64], but few have explored controlled growth in large scale substrates, which would be useful in the large scale fabrication of carbon nanotube based electronics devices in future. A series of experiments is to be carried out to grow vertically-aligned carbon nanotubes at predefined positions on metal electrodes. The objective is to design and test the entire fabrication process on 4-inch wafers, which could be scaled up to current industry scale. Carbon nanotubes are designed to grow on a metal layer, which makes them easily accessible electrically. Thousands of vertically aligned
carbon nanotubes sites are to be grown on every metal line end. The configuration may have many applications, such as vertical interconnects between layers, vertical channels of three dimensional chips, field emission devices and probes for biosensing chips.

4.2 Experiment and Results

This experiment was to fabricate large scale vertically-aligned carbon nanotube array on a 4-inch wafer. Carbon nanotubes were grown at the predefined position on the metal lines, Figure 4.1 shows a schematic diagram of the process. The spacing between every carbon nanotube site is controlled by patterning the position of the catalyst film. The diameter and length of carbon nanotubes were also controlled. Insulating layers were coated after CNT growth, and the electrical property was tested. The final product is a 4-inch wafer with an array of hundreds of vertically-aligned carbon nanotube sites. Biosensing, as one of the applications, was tested on the final product.

Figure 4.1 Schematic diagram of the fabrication process of carbon
nanotube based microelectrodes array (a) Silicon wafer (b) Photolithography patterning of metal electrodes (c) Photolithography of patterning of catalyst (d) Carbon nanotubes growth by PECVD process (f) Insulating layer coating

Intrinsic silicon wafer with high resistivity was selected to be the substrate because of its high resistivity (figure 4.1(a)). Wafers with a few microns insulating layer such as SiO$_2$ and Si$_3$N$_4$ have also been evaluated for the experiment. However, these wafers could not withstand the thermal stress caused by the high temperature CVD process, and top layer peeling off has been observed (figure 4.2(a)). Also those wafers with insulating layer tended to result in electric arcing (figure 4.2(b)) during the plasma process. So high resistivity intrinsic silicon wafers, which don’t have the peel-off and arcing problems, were found to be more suitable for this experiment.

Figure 4.2 Process problems with insulating layer coated wafer. (a) Peeling off of 2 $\mu$m Si$_3$N$_4$ layer during CVD process (b) Arcing during the plasma
process

4.2.1 Metal layer patterning

The first process step was to make metal electrodes on the 4-inch silicon wafer. Every electrode is basically a metal line from the periphery of the wafer, where the wirebond pads are located, to the center region, where a carbon nanotube array is located. A 9 X 9 array was designed, with every site having 5 electrodes.

The mask for the first layer metal was designed using Cadence software. Figure 4.3 shows the image of the mask design. There are 405 (9 X 9 X 5) metal lines for carbon nanotubes, which were grown at the end of every metal line. There are three additional metal lines, which are connected to the three big round-shape ground pads. Thus there are a total of 408 metal lines on the wafer. The active region is 70 X 70 mm square, with 4-inch diagonal lengths. There are 102 bond pads on each of the 4 peripheral sides.
Photolithography was used to pattern the first layer metal. Photoresist AZ5412 was used.

Photoresist AZ5412 was spun on the wafer by a spinner (Figure 4.4). 5ml photoresist was dropped on the center of wafer, and then the wafer
was spun at 6000 rpm for 1 minute. After that the wafer was baked in an oven at 90°C for 20 minutes. The thickness of photoresist layer prepared in this way was about 1.2 μm. Mask aligner was used for the exposure process. After exposure, the wafer was rinsed in diluted AZ developer for 1 minute. The diluted AZ developer was made up of pure AZ developer and DI water in the ratio 2 : 1. After developing, the wafer was rinsed in DI water and blown dry by N₂ gas. The wafer was then loaded into an oven at 90°C for 20 minutes for post baking.

Ti was chosen to be the material for the metal interconnects, due to its high melting point (1668 °C) and good contact property with carbon nanotubes [62-65]. Ti was coated on the wafer by e-beam evaporation at 1 X 10⁻⁶ mbar; the thickness of Ti layer is 150 nm.

Figure 4.5 shows the optical pictures of the Ti electrode layer. Figure
4.5 (a) shows one site of Ti electrodes, which has 5 Ti lines. The width of the line is 20 \( \mu m \). Carbon nanotubes were grown at each end point (20 X20 \( \mu m^2 \)) of the metal lines. The distance between two neighboring metal line end points is 80 \( \mu m \). There is a 9 X 9 array of such sites at the center region of the wafer. Figure 4.5 (b) shows the bond pads connection to each of the metal lines. Each pond pad is 300 X 300 \( \mu m^2 \) in size. A probe station was used to test the resistance of the metal line. The resistance was measured to be from 0.4 k\( \Omega \) to 1 k\( \Omega \), which includes the contact resistance between two tungsten probes and titanium metal. So the resistance of the metal lines is expected to be in the order of hundreds of Ohms.

### 4.2.2 Catalyst patterning

![Catalyst pattern](image)

Figure 4.6 Optical image showing the catalyst pattern by photolithography, the scale bar is 20 \( \mu m \).

The catalyst layer is the second layer to be patterned. The position of
the catalyst is at the end of every metal line (figure 4.6). Every catalyst dot is 20 X 20 μm² square. The mask for the catalyst was designed using Cadence software, and mask aligner was used to do the second layer lithography.

Nickel and iron were tried as catalyst material respectively. Thermal evaporation was used to coat the catalyst. In the first experiment, 5 nm of nickel was coated patterned as catalyst according to the previous experiment in chapter three. However, no carbon nanotubes were grown with keeping all other parameters the same as previous experiments described in chapter three. The only process difference is that there was a catalyst lift-off process in the later experiment. A thicker catalyst layer may be needed in a patterned catalyst process than in an entire coating process. So a series of experiments was carried out to calibrate the process parameters. The thickness of the catalyst was found to be different from previous experiments in order to have carbon nanotube growth. Optimum thickness for nickel and iron are found to be 20 to 25 nm.

4.2.3 Carbon nanotube growth

After catalyst patterning, experiments were carried out to grow multi-walled carbon nanotubes using PECVD. The wafer size is 4-inch, it is reasonable that most of the process parameters are different from those of the 5 X 5 mm² die. A series of experiments was performed to achieve the
optimum condition for carbon nanotubes growth.

**Temperature**

The temperature during CVD plays an important role. In theory, CNT growth temperature should be the same irrespective of wafer size. However, in this experiment the CVD heater is only 3 cm diameter, which is smaller than the wafer size. So it was found that 4-inch wafer requires higher heater power compared with 5 X 5 mm² dies. The temperature at the center of the 4-inch wafer needs to be maintained at a higher degree compared with 5 X 5 mm² dies. Larger wafer area has larger thermal mass and higher heat dissipation. SEM image (figure 4.7) shows no CNT growth at 730°C with all other parameters the same. It was found that the heater center temperature needs to be above 800°C to achieve carbon nanotube growth.

Figure 4.7 CVD growth result of carbon nanotube on 4-inch wafer at 730°C
Plasma power

Plasma power is another important parameter to achieve straight vertically-aligned carbon nanotubes. 4 inch wafer was found to require much higher DC voltage and current for plasma. Increasing the area of the die increases the capacitance of it. In order to have a similar voltage drop at the sheath region of plasma, it is needed to have more charges, which may require a high DC voltage and current consequently. Figure 4.8 shows the growth result with the same plasma power as 5 X 5 mm$^2$ die (Plasma voltage is 520V, current is 43 mA) and all other parameters were the same. It shows carbon nanotubes are not vertically aligned. The electrical field force was not enough to make all carbon nanotubes grow in the vertical direction. It was found that the plasma current needed to be above 80 mA to have all carbon nanotubes growing straight upwards.

Figure 4.8 CVD growth result of tapered amorphous carbon growth on 4-inch wafer with a lower plasma power
Gas flow rate

Flow rate of C$_2$H$_2$ is also very important to grow carbon nanotubes, because C$_2$H$_2$ is the carbon source in the reaction. For the first several experiments, C$_2$H$_2$ flow rate is the same as that of 5 X 5 mm$^2$ dies, however, carbon nanotubes grown were found to be not of the expected morphology (especially the diameter). Figure 4.9 shows one example of the results. It was not clear how the flow rate of C$_2$H$_2$ actually affects the growth. So several experiments were carried out with reduced and increased the flow rate of C$_2$H$_2$. It was found that a higher flow rate of C$_2$H$_2$ is needed to have acceptable carbon nanotube growth.

Figure 4.9 CVD growth result of carbon nanotube on 4-inch wafer with a lower flow rate of C$_2$H$_2$

After a series of calibrations for all the major parameters, the optimum
condition to grow carbon nanotube on titanium on a 4-inch wafer was achieved. Figure 4.10 shows an example of the successful growth of carbon nanotubes on titanium electrodes. The CVD process parameters are listed as below:

Flow rate of NH$_3$ is 60 sccm
Flow rate of C$_2$H$_2$ is 12 sccm
Pressure is maintained at 8 mbar
Temperature is maintained at 800 °C
Plasma voltage is 710V, current is 100 mA
Duration of growth is 15 minutes

Multi-walled carbon nanotubes were successfully grown on the Ti metal line end (figure 4.10). The length of the carbon nanotube is about 20 to 25 μm, which could be controlled by the growth time. It was counted that there were hundreds of multi-walled carbon nanotubes on each 20 X 20 μm$^2$
growth points. From the electrical point of view, the carbon nanotubes form hundreds of parallel conducting paths, which have a reduced resistance compared with an individual path. Also from a statistical point of view, the hundreds of carbon nanotube conducting paths reduce the variance of electrical property at each point. The titanium electrode with carbon nanotubes was characterized with the best-case CNT-Ti line resistance being approximately 4.3 kΩ and 10 kΩ on the average.

4.2.4 Insulating layer coating

Liquid spin-on glass (SOG) was chosen to coat a layer of the SiO₂ on the wafer. 3 ml SOG was dropped on the center of the wafer, which was then spun at 1000 rpm for 30 seconds by an electrical spinner. Spin on glass is soluble in acetone when it is still in liquid form. So the periphery of the wafer was immediately cleaned using a cotton bud rinsed with acetone. All the bond pads regions were exposed while other area was covered with SiO₂. The wafer was then kept in an oven at 60°C for one week for curing.
The final product is shown in figure 4.11. The center ellipse is the heating zone during the CVD process, the heating element of the CVD system is about 3 cm in diameter. The SiO$_2$ covered region is in light blue color. Bond pads at the periphery are exposed.
Figure 4.12 SEM image of Carbon nanotube-titanium electrodes testing wafer after SiO$_2$ coating

The thickness of the SiO$_2$ layer is about 1 $\mu$m after curing. Figure 4.12 shows the SEM image of one site of the carbon nanotube array. It shows that the shorter carbon nanotubes are buried under the SiO$_2$ layer. The longer carbon nanotubes are exposed, and the number of exposed carbon nanotubes at each point is twenty on average.

Evaporation of SiO$_2$ was also investigated to coat the insulating layer
before spin-on glass was chosen. It showed that SiO₂ evaporation also coated a layer over the entire wafer, which also covered the carbon nanotubes (figure 4.13). The SiO₂ layer on carbon nanotubes was found to be difficult to remove. Patterned SiO₂ coating by lithography was not considered in this case, because the CNT length (more than 10 μm) is larger than the resist layer thickness. So the spin-on glass process is a better option for forming the insulating layer.

Figure 4.13 SiO₂ coating on carbon nanotube by evaporation

4.3 Summary

Having the carbon nanotubes on 4-inch substrate in a controlled manner is achieved by a direct growth method. The position is defined by catalyst patterning. The direction of carbon nanotube is controlled by the electric field of the plasma. The diameter and length are controlled by the catalyst and growth duration. Carbon nanotubes are grown on titanium
electrodes, which enable many electrical applications, such as carbon nanotube based vias, vertical channels and probes. Biosensing, as one the potential applications, has been investigated [66]. The control over the fabrication process at such large scale also makes it a possible path for industrial production in future nanotube integrated electronic devices.

Process parameters for carbon nanotubes growth on 4-inch wafers are different from those for millimeter size die. Higher plasma power and CVD heater temperature are needed for large scale growth. A thicker catalyst layer is also needed for patterned growth.

There is still room for further improving the controlling of the fabrication process, such as exact control of the number of carbon nanotube on each growth point and the uniformity of the electrical property of the carbon nanotubes. The controlled direction of carbon nanotube growth in this experiment is confined in the vertical axis (perpendicular to wafer surface), which may have potential application in novel three dimensional electronic devices [67]. The control of the positioning of nanotubes in the lateral direction is also important and a great technology challenge; this issue is explored in the next two chapters.
Chapter Five -- Positioning of Carbon Nanotubes by Patterned Deposition

5.1 Objective

Practical application of carbon nanotubes requires the controlled and predictable assembly of carbon nanotubes on wafer surface. Controlled positioning by direct growth has been explored in Chapter Four. However, the growth direction is limited by the electric field direction of the plasma. Previous research work proposed various post-synthesis methods to deposit carbon nanotubes in a desired way [20-22]. In this chapter, controlled assembly of carbon nanotubes by patterned deposition is to be explored. Carbon nanotubes are to be deposited laterally with controlled number, position and direction on a chemically modified silicon wafer surface. The objective of this experiment is to achieve single carbon nanotube deposition on the wafer surface with controlled position and direction.

5.2 Experiment and results

The experiment procedures are described in figure 5.1. Silicon die with
a thermal oxide layer of 400 nm was first coated with 3 percent PMMA by a spinner at 6000 rpm for 1 minute. It was then patterned by standard electron beam lithography (figure 5.1(a)). The test die was then cleaned by oxygen plasma for 10 seconds. After cleaning it was immediately put into a vacuum chamber and exposed to ethylenediamine (EDA, C$_2$H$_4$(NH$_2$)$_2$) vapor for 15 minutes, and then exposed to aminopropyltriethoxysilane (APTS) vapors for 90 seconds. [31]

Figure 5.1 Schematic of Carbon nanotubes being deposited on SiO$_2$ surface by patterned PMMA trench

After that, the die was annealed in an oven at 120 °C for 25 minutes to achieve the full condensation of APTS. Subsequently the die was put into the vacuum chamber again and exposed to trifluoroacetic acid vapors for 20 minutes to have the APTS tracks fully protonated (to convert -NH$_2$ to -NH$_3^+$). The die was then immediately immersed in a freshly prepared carbon nanotube suspension for 24 hours.
During the immersion, carbon nanotubes were randomly attached to the surface of the die due to amino-functionalized molecules bonding. There was a chance that some carbon nanotubes fall into the PMMA trench and attach to the chemically modified SiO$_2$ surface (figure 5.1 (d)). In this way, carbon nanotubes were directionally attached to the die surface. The die was finally rinsed with DI water for 1 minute, acetone for 1 minute, and ethanol for 1 minute successively. This was to wash away the resist layer, and only the carbon nanotubes, which had been attached to the die surface, were left on the surface with predefined position and direction (Figure 5.1 (e)).

The carbon nanotube suspension was obtained by sonicating 2.5 mg of purified multi-walled carbon nanotube powder in 25 ml of N-methylpyrrolidone for 4 hours. The suspension was then centrifuged at 5000 rpm for 30 minutes to remove the aggregated nanotubes. The supernatant was collected and resonicated for 17 hours.

A test structure was designed to make PMMA trenches using electron beam lithography. As shown in figure 5.2, the test pattern consists of long trenches with width from 0.2 to 5 micron in both v and u directions. The optimum line width to pattern single carbon nanotube was to be studied.
Figure 5.2 Testing patterns for PMMA trenches

The experiment result shows that a 0.5 to 1 \( \mu \text{m} \) wide PMMA trench was able to attach a single carbon nanotube on the surface. In figure 5.3, it could be seen that a single carbon nanotube was deposited at the predefined position in a straight line, where the trench width for this patterning is 0.5 \( \mu \text{m} \).

Figure 5.3 SEM image shows single carbon nanotube deposited in
predefined location by monolayer assembly in 0.5 μm PMMA trench

In a 2 μm wide PMMA trench (figure 5.4), no carbon nanotubes could be found. As shown in figure 5.4, it could be seen that there are a number of particles attached to the surface. The particles probably are the carbonaceous material from the carbon nanotube powder produced during the arc discharge process. It could be one possible reason that the particles occupy the surface area, so carbon nanotubes could not attach to the surface. In a narrower PMMA trench, due to the size limitation, no junk particle could fall into the trench, so the narrower PMMA trench becomes more effective in attaching carbon nanotube to the surface. Figure 5.5 shows that the result for several PMMA trenches with width larger than 2 μm. Again, no carbon nanotube could be found on the surface.

Figure 5.4 SEM image shows no carbon nanotube could be found in 2 μm PMMA trench
Figure 5.5 SEM image shows no carbon nanotube could be found the PMMA trenches larger than 2 μm.

Figure 5.6 SEM image of the carbon nanotube positioned in 1 μm PMMA trench (a) Low magnification (b) High magnification

The length of the PMMA trench is more than 50 μm. It also could be seen from the SEM image that the carbon nanotube positioned could be as
long as the trench length (figure 5.6(a)). However, the specified length of the carbon nanotubes bought is about 5 to 10 \( \mu \text{m} \). Higher magnification SEM image on some part of the tube (figure 5.7) reveals that the ‘single’ long carbon nanotube actually consists of many short carbon nanotubes connected together in tandem. It is also observed that there are small junk particles attached to the tube wall. These particles are found to be difficult to be cleaned, which could be one of the drawbacks of this deposition method.

Figure 5.7 SEM image showing that carbon nanotubes positioned in tandem along the PMMA trench

5.3 Summary

Carbon nanotube can be patterned to predefined position by chemically
modifying the silicon wafer surface. Gas-phase silane deposition was used to form an adhesion layer. Carbon nanotubes could be deposited laterally at predefined locations using such silanized patterns. PMMA trench width was found to be important to achieve aligned individual carbon nanotube deposition. A narrower PMMA trench is more effective in achieving aligned carbon nanotube deposition. For individual carbon nanotube deposition, the PMMA trench width needs to be narrower than 1 μm. Metal electrodes could be patterned on the carbon nanotubes subsequently. This technique provides a possible way to pattern nanotube based structures on a large scale. Further work still need to be carried out to reduce the number of the organic particles being deposited.
Chapter Six – Controlled Positioning of Carbon Nanotubes by ac Dielectrophoresis

6.1 Objective

In order to use carbon nanotubes for electron transport as interconnects or channels in FETs in the next generation of devices, challenges still need to be overcome. The precise positioning of a nanotube between electrodes needs to be addressed. Dielectrophoresis has been experimented to control the position of carbon nanotubes. Work has been done to achieve a bulk control of carbon nanotubes aligned at the electrode gap. This chapter will explore the controlled positioning of carbon nanotubes by dielectrophoresis in more precise aspects, including the density of carbon nanotubes being aligned, the direction, and the effect of electric field. The objective is to gain control over carbon nanotube assembly between electrodes with a single tube precision.
Chapter 6 – Controlled Positioning of Carbon Nanotubes by ac Dielectrophoresis

6.2 Methodology

Silicon dies with 400 nm SiO₂ top layer and a titanium electrode layer were used in this experiment. Figure 6.1 shows a schematic experiment set up. A probe station was used to make connection from the ac power supply (HP33120A Waveform Generator) to the electrodes on the test die. A small volume (less than 10 micro liter) of carbon nanotube suspension was dropped on the die surface using a microsyringe, and ac power supply was immediately turned on. The ac power was turned off when the drop of the suspension had dried, a process which usually takes less than 30 seconds.

![Figure 6.1 Schematic of the experiment set up for dielectrophoresis](image)

Figure 6.1 Schematic of the experiment set up for dielectrophoresis

The dielectrophoretic force on a particle of dielectric function \( \varepsilon_1 \) with radius \( r \) in a medium of dielectric function \( \varepsilon_2 \) is
\[ F_{\text{DEP}} = 2\pi \varepsilon_1 \Re \left| K(\omega) \right| r^3 \nabla E_{\text{rms}}^2 \]  

(1)

where \( E \) is the electric field (with rms standing for root-mean square) and \( K \) is the Clausius-Mossotti factor (the nanotube can be considered to be quasi-spherical). This factor depends on the difference in the dielectric constants of the particle and the medium [68].

\[
\Re \left| K \right| = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} + \frac{3(\varepsilon_2 \sigma_2 - \varepsilon_1 \sigma_1)}{\tau_{\text{MW}}(\sigma_2 + \sigma_1)^2(1 + \omega^2 \tau_{\text{MW}}^2)} 
\]

(2)

The dielectrophoretic force consists of the dielectric and Coulomb forces. The former arises from gradients in the permittivity (first term) and the latter from gradients in the conductivity \( (\sigma) \) (second term). The first term on the right hand side of (2) shows that the higher dielectric function materials are pulled into higher field regions. For a tube with a cylindrical shape, the dielectrophoresis force is

\[
F_{\text{DEP}} = \frac{\pi d^2 l}{8} \varepsilon_1 \Re \left( \frac{\varepsilon_i^* - \varepsilon_j^*}{\varepsilon_i^* + (\varepsilon_i^* - \varepsilon_j^*)L} \right) \nabla E_{\text{rms}}^2 
\]

(3)

where \( \varepsilon_i^* \) and \( \varepsilon_j^* \) are the complex dielectric constants of the tube and the
surrounding liquid, \( \varepsilon \) and \( \sigma \) are the corresponding real parts of the dielectric constants and conductivities, \( L \) is the depolarization factor, and \( d \) and \( l \) are the diameter and length of the tube [69].

6.3 Experiment and results

6.3.1 CNT suspension preparation

The carbon nanotubes used in this experiment were bought from SES Research. They were produced by arc discharge method and in powder form (figure 6.2).

![Figure 6.2 Arc discharge carbon nanotube powder produced by SES Research](image)

A carbon nanotube suspension was made by dispersing some carbon nanotube powder in dichloroethane solvent. Ultrasonication (figure 6.3) was used to separate bundles of carbon nanotubes into isolated carbon
nanotubes in the solvent. The objective of the dispersion is to achieve a uniform suspension, in which most of the carbon nanotubes are isolated. The solution should also be stable, which means that the carbon nanotubes are not going to aggregate or sink immediately after ultrasonication is stopped.

In previous studies, many different types of solvent including DI water, isopropyl alcohol (IPA), acetone, trichloroethane (TCE) and dichloroethane (DCE) have been tried to prepare the carbon nanotube suspension. DCE was recommended to be one of best solvents for carbon nanotubes dispersion [70]. In this experiment, carbon nanotubes were tried to be dispersed in DI water, IPA and DCE. It was found that DI water and IPA could not uniformly disperse carbon nanotubes, because carbon nanotube sediments were observed at the bottom of the container even after long-time (more than 24 hours) ultrasonication. Uniformly dispersed carbon
nanotubes suspension was achieved using DCE. 2.5 mg carbon nanotube powder was added into 25ml DCE solvent in a sealed bottle. The mass of the carbon nanotubes powder were measured precisely by the Precisa XB220A (Microbalance, figure 6.4), which has a precision of 0.1mg.

Figure 6.4 Weighing machine for CNT powder measurement

The sealed bottle was then kept in an ultrasonic bath for 24 hours. The suspension after ultrasonication was black in color with no carbon nanotube sediment at the bottom of the bottle. The carbon nanotube-DCE suspension prepared in this way was stable for a long time. No aggregation was observed after three months.

6.3.2 The effect of the concentration of CNT suspension on dielectrophoresis

As the objective of the experiment is to achieve controlled positioning of
carbon nanotubes between electrodes, the density of carbon nanotubes between electrodes is a major target to be controlled. The experiment showed that the concentration of the carbon nanotube suspension was a crucial factor, which will affect the density of carbon nanotubes between electrodes.

Round shape titanium electrodes with 1.5 μm spacing was used in this series of experiments (figure 6.5).

Figure 6.5 Round-shape electrode structure for carbon nanotube dielectrophoresis. The scale bar is 5 μm

Four experiments have been carried out with different concentrations of carbon nanotube-DCE suspension (figure 6.6). The preparation method of the suspension was described in 6.3.1.
Figure 6.6 Carbon nanotube-DCE suspension with different concentration, which from left to right is 0.5mg/25ml, 1mg/25ml, 2mg/25ml and 2.5mg/25ml.

Other parameters of the experiments are as follows:

- Volume of DCE solvent: 25ml
- Ultrasonication duration: 24 hours
- Ac power supply: square wave 5 Vpp, 100 kHz
- Duration of dielectrophoresis: 30 seconds

The result is shown in figure 6.7. The first experiment was carried out using the most concentrated solution (figure 6.7(a)), it could be seen that carbon nanotubes as well as some junk particles were attracted to the circle shape spacing between the two electrodes. The carbon nanotubes are dense and formed an almost continuous layer on the die surface. The concentration of carbon nanotubes was too high in this experiment.
In the second experiment (figure 6.7(b)), it could be seen that carbon nanotubes were attracted to the spacing between the two electrodes. Compared with the first experiment, the density of carbon nanotubes is reduced. However, the carbon nanotubes are still dense and formed an almost continuous layer at the gap region. The concentration of carbon nanotubes is still too high to achieve isolated tube aligned between electrodes.
With other parameters unchanged, the third experiment was carried out with reduced carbon nanotube concentration (figure 6.7(c)). It could be seen that carbon nanotubes are attracted to the spacing between the two electrodes. Compared with the previous two experiments results, the density of carbon nanotubes is much reduced. Instead of a continuous layer of carbon nanotubes, individual carbon nanotube is observed between the electrodes. The distance between two neighboring individual carbon nanotubes is about 0.5 μm, which is still a bit small. So one more experiment was carried out with reduced carbon nanotubes concentration. The result is shown in figure 6.7(d). It could be seen that carbon nanotubes are attracted to the spacing between the two electrodes. Compared with the previous three experiments, the density of carbon nanotubes is much reduced. Isolated carbon nanotube is observed between the electrodes. The distance between two neighboring individual carbon nanotubes is more than 2 μm, which could be an acceptable distance for the next experiment.
To understand the electric field better for various electrode structures, the electric field was simulated using the Maxwell 3D finite element analysis software (Ansoft Corporation). The Ti electrodes and the SiO$_2$ substrate were included in the simulations. Neumann boundary conditions were assigned to the outside edges of the problem region and Dirichlet boundary conditions were assigned to the powered electrodes.

The simulation result for the round-shape electrode structure is shown in figure 6.8. Compared with the experiment results, carbon nanotubes are attracted to the higher electric field intensity region and the tube axis follows the electric field vector direction.
6.3.3 Dielectrophoresis on two-electrode structure

In this experiment, controlled positioning of carbon nanotubes between two electrodes by dielectrophoresis was carried out on the structure in figure 6.9. The objective was to place a single carbon nanotube bridging the two electrodes.

![Two electrodes structure for carbon nanotube dielectrophoresis. The scale bar is 10 μm](image)

Figure 6.9 Two electrodes structure for carbon nanotube dielectrophoresis. The scale bar is 10 μm

The simulation of electric field of the two-electrode structure is shown in figure 6.10. The figure shows that the region between two electrodes has the highest electric field intensity. So it was expected carbon nanotubes are driven by the dielectrophoretic force to that high field region. The tube axis was expected to follow the electric field vector direction.
In the previous experiment, it is observed that there were some junk particles on the die surface. The particles are suspected to be carbonaceous material produced alongside the carbon nanotubes during the arc discharge synthesis process. To reduce the number of particles in this experiment, the carbon nanotube-DCE suspension was centrifuged (figure 6.11) at 10000 rpm for 30 minutes to remove the aggregated nanotubes. The supernatant was collected and resonicated for 24 hours.

Figure 6.11 Centrifuge machine Hettich Mikro120
Dielectrophoresis was carried out and the parameters are as follows:

- Mass of carbon nanotubes: 0.5 mg
- Volume of DCE solvent: 25ml
- Ultrasonication: 24 hours
- Centrifugation: 10000 rpm, 30 minutes
- Resonication of the supernatant: 24 hours
- Ac power supply: square wave 5 Vpp, 100 kHz
- Duration of dielectrophoresis: 30 seconds

![Figure 6.12 SEM image of CNT after dielectrophoresis on the two electrodes structure, ac power supply: square wave 5 Vpp, 100 kHz]

The result is shown in figure 6.12. It could be seen that an individual carbon nanotube has been attracted to the gap between the two electrodes. A single carbon nanotube aligned between two electrodes has been achieved. Compared with the previous experiments, the density of particles was much reduced by the centrifugation.
One more experiment has been carried out with reduced electric field. The parameters of the dielectrophoresis are as follows:

- Mass of carbon nanotubes: 0.5 mg
- Volume of DCE solvent: 25ml
- Ultrasonication: 24 hours
- Centrifugation: 10000 rpm, 30 minutes
- Resonication of the supernatant: 24 hours
- Ac power supply: square wave 1 Vpp, 100 kHz
- Duration of dielectrophoresis: 60 seconds

Figure 6.13 SEM image of CNT after dielectrophoresis on the two electrodes structure, ac power supply: square wave 1 Vpp, 100 kHz

In this experiment, the duration of dielectrophoresis was increased, because it was observed that the drop of carbon nanotube-DCE suspension dried at a slower speed than previous experiments, which may result from the decreased voltage of the ac power. The dielectrophoresis
result is shown in figure 6.13. It could be seen that individual carbon nanotube has been attracted to the gap between the two electrodes. Single carbon nanotube aligned between two electrodes has been achieved. Compared with the previous experiments, the density of junk particles was much reduced. The reduction of the density of particles in the latter experiment may result from the reduced ac voltage. It is reasonable that fewer particles have been attracted to the electrodes under a smaller electric field. It is also noticed that the direction of the carbon nanotubes aligned between electrodes may not be parallel to the electric field vector direction, and this may also relate to the reduction of electric field.

6.3.4 Dielectrophoresis on four-electrode geometry

Controlled positioning of carbon nanotubes on a four-electrode structure by dielectrophoresis has been carried out. Optical picture of the electrodes geometry is shown in figure 6.14. The objective was to have single carbon nanotubes being aligned between the two electrodes, which were connected to the ac power supply.
Figure 6.14 Optical picture of the four electrodes structure for carbon nanotubes dielectrophoresis. The scale bar is 2 μm

Simulation of electric field of the four-electrode geometry is shown in figure 6.15. The highest electric field intensity (around $3.2 \times 10^6$ V/m) appears at the vertices of the two electrodes, which are connected to the ac power supply. The vertices of the other two floating electrodes have lower electric field intensity (less than $3.9 \times 10^5$ V/m). So it was expected that carbon nanotubes would be driven by the dielectrophoretic force to that high field region. The tube axis was expected to follow the electric field vector direction, which is parallel to the horizontal direction. If there is only one carbon nanotube aligned in that region, that particular tube is going to be positioned from the vertex of left electrode to the vertex of the right electrode.
Figure 6.15 Simulation of the electric field intensity for the four-electrode geometry

In this experiment, the parameters of the dielectrophoresis are as following:

- Mass of carbon nanotubes: 0.5 mg
- Volume of DCE solvent: 25ml
- Ultrasoundication: 24 hours
- Centrifugation: 10000 rpm, 30 minutes
- Resonication of the supernatant: 24 hours
- Ac power supply: square wave 5 Vpp, 100 kHz
- Duration of dielectrophoresis: 30 seconds
Figure 6.16 SEM image showing a single carbon nanotube aligned between two electrodes in four-electrode geometry

The result is shown in figure 6.16. SEM shows that a single carbon nanotube was aligned from the vertex of the left electrode to the vertex of the right electrode. The experiment result matches the expectation from the electric field simulation result. Low concentration carbon nanotube-DCE suspension was used, and centrifugation was carried out to further purify the suspension. Hence the junk particle density appears low as shown in the SEM image.

The I-V Characteristic of the carbon nanotube was measured using the Keithley 4200 semiconductor characterization system. Figure 6.17 shows the I-V curve. It could be seen from the figure that the resistance of the carbon nanotube is around 30 kΩ, which is similar to the resistance value of multi-walled carbon nanotubes measured by other research groups [71].
Hence, these results show that controlled CNT positioning with good electrical contact can be achieved using the dielectrophoresis approach described in this chapter.

Figure 6.17 I-V characteristic of the carbon nanotube between two electrodes

### 6.4 Summary

Dielectrophoresis provides a way to achieve controlled positioning of carbon nanotubes and make them be easily addressed and connected to the macroscopic outside world. Comparison between the simulation and experimental results shows dielectrophoretic force drives carbon nanotube to the higher electric field intensity region. The concentration of carbon nanotube suspension affects the density of the carbon nanotubes being aligned. Electric field with smaller magnitude attracts fewer carbon nanotubes as well as junk particles. With a proper electrode configuration
and carbon nanotube solution concentration, carbon nanotube can be positioned between electrodes with single tube precision. One of the major issues is the cleanliness of this process; junk particles from the carbon nanotube powder contaminate the suspension. Centrifugation of the suspension was found to be effective in reducing the junk particle density. By manipulating the electrode geometry, the electric field could be modified in intensity and direction, and this paves the way for using ac dielectrophoresis to align nanostructures in complex circuits. Future work could be carried out to dielectrophoretically position carbon nanotubes for many potential applications, such as digital sensing, interconnects [18] and FET structures for logic circuits.
Chapter Seven – Conclusions

Carbon nanotube CVD growth process is the decomposition of hydrocarbon with the aid of transition metal catalysts. The diameter of the carbon nanotube mainly depends on the size of the catalyst particle, which is related to the thickness of the coating layer, the temperature during annealing, and the substrate material. By properly tuning these parameters, multi-walled carbon nanotubes could be grown with desired diameter and length.

For the PECVD growth process, the nanotubes grow along the electrical field direction of the sheath of the plasma, which is perpendicular to the local surface plane of the test die. The growth direction of carbon nanotubes could therefore be controlled.

Carbon nanotubes arrays growth on Ti electrodes on 4-inch wafer with controlled position, direction and length was achieved by PECVD. Process parameters for carbon nanotube growth on 4-inch wafers are different from those for millimeter size die. Higher plasma power, CVD heater power and thicker catalyst layer are needed for large scale growth. The structure may have many potential applications, such as carbon nanotube based vias, vertical channels for FET and probes for biosensing of living cells. The control over the fabrication process at this large scale makes it a possible path for industrial production in future nanotube integrated electronics.
devices.

Carbon nanotubes have also been deposited laterally at predefined location on silanized SiO$_2$ surface. PMMA trench width was found to be important to achieve aligned individual carbon nanotube deposition. Individual carbon nanotube deposition was only found in those positions where the PMMA trench width is narrower than 1 $\mu$m. Junk particles generated during the many process steps are one drawback of this method. Further work still needs to be carried out to reduce the contamination.

Dielectrophoresis provides a way to achieve controlled positioning of carbon nanotube between electrodes, so that they are easily addressed and connected to the macroscopic outside world. Comparison between the simulation and experimental results shows dielectrophoretic force drives carbon nanotube to the higher electric field intensity region. With proper electrode configuration and carbon nanotube solution concentration, a carbon nanotube can be positioned between electrodes with single tube precision. Centrifugation of the suspension was found to be effective in reducing the junk particle density.

In conclusion, the objectives of the M.Eng project have been met. It has also evoked new curiosity and created much scope for further experimentation. This documentation will serve as a basic exploration on
the controlled methods of fabrication and assembly of carbon nanotubes based nanostructure as future nanoscale building blocks. It would facilitate and contribute to further developments in the field of carbon nanotube-based nanoscale devices.
References

References


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