Deposition of carbon layers from cyclohexane by thermal Chemical Vapor Deposition

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DEPOSITION OF CARBON LAYERS FROM CYCLOHEXANE BY THERMAL CHEMICAL VAPOR DEPOSITION

A Thesis
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering in The Department of Electrical and Computer Engineering

by
Bharath Thiruvengadachari
B.E, Kuvempu University, India, 2001
May 2005
Dedicated to my family
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The overall aim of this thesis is to deposit carbon layers by thermal Chemical Vapor Deposition (CVD) and investigate the effects of process parameters on the morphology and structure of the deposited carbon layers. Cyclohexane (C₆H₁₂) hydrocarbon is the precursor material used as the source of carbon. A 20% Cu- 80% Ni alloy, deposited by RF magnetron sputtering and annealed at the growth temperature either in an argon flow or in 10% hydrogen-90% argon flow, is used as a catalyst prior to carbon film deposition by CVD. The CVD temperature is varied between 550 °C and 800 °C. The Cu-Ni film thickness for CVD is varied from 2 nm to 80 nm. Carbon layers obtained after each CVD growth run of 12 min are characterized by scanning electron microscopy (SEM). The most likely temperature for carbon nanotube (CNT) growth seems to be 725 °C. Growth of fibers and rods is found to occur on CuNi films deposited on oxide coated silicon substrates and not on silicon substrates. The Cu-Ni film on oxide should not be more than 15 nm thick for argon anneal to produce CNTs upto 150 nm in diameter. Cu-Ni catalytic films of thicknesses 6 nm, 12 nm and 24 nm on patterned oxidized substrates are annealed in Ar and Ar-H₂ flows for 15 and 30 min at 760 Torr. Smallest size catalyst particles are observed on oxide coated substrates. CVD growth is carried out on the 6 nm and 12 nm catalytic Cu-Ni films for 12 min on oxide coated substrates at 725 °C in Ar-H₂ atmosphere. In the first case, 50 nm diameter carbon fibers are produced while 160 nm diameter carbon fibers are observed for the 12 nm thick Cu-Ni film. Transmission electron microscopy (TEM) analysis on the carbon fibers revealed multi-walled structures, 50 nm and 130 nm in diameters indicating the growth of CNTs comparable to
the average size of the catalyst particles after annealing. Resistivity measurements on the
carbon layers on 6 nm and 12 nm Cu-Ni films show sheet resistivity values of 293
Ω/square and 85 Ω/square respectively.
1. INTRODUCTION

1.1 Background

Since the discovery of carbon nanotubes by Sumio Iijima in 1991 [1], there have been a large number of papers detailing the research of this fascinating new form of carbon. Previously, pioneering work in this field was done around 1985 by Kroto, Curl and Smalley [2] who conducted experiments on the vaporization of carbon. They noticed that when graphite, a form of carbon, was vaporized by a laser in the presence of helium, 60 carbon molecules clustered in closed round shapes called buckyballs or fullerenes (C_{60}) in the deposits formed. Molecular structure of a buckyball is shown in Fig. 1.1.

![Buckyball (C_{60}) structure.](image)

The fullerene structures were highly stable and had not been observed until then. However, the quantity of the fullerenes produced in the experiment was very small and consequently led to research directed towards producing larger quantities. This was achieved by Huffman [3] at the University of Arizona and Kratschmer at the Max Planck Institute for Nuclear Physics, Germany, who published the first paper on mass production
of $C_{60}$ in 1990. Their method used a simple carbon arc instead of a laser to vaporize graphite. The soot deposited on the side walls of the vessel, when dissolved in benzene and dried, gave macroscopic quantities of $C_{60}$. Carbon nanotubes were first discovered by Iijima in 1991, who was an electron microscopist at NEC laboratories in Japan. Using TEM, he observed tube-like hollow carbon structures, which were deposited along with soot on the cathode in an arc discharge process. These structures were different from the four structures of carbon previously seen – crystalline material like graphite and diamond and non crystalline material like charcoal and buckyballs. The hollow structures were made of multiple rolled up sheets of graphite usually closed at both ends by caps which have six pentagonal rings each. The rolled up graphite sheets were made up of arrays of hexagons linked together with carbon atoms at the corners of these hexagons. These tubes had their diameters in nanometers and a length of nearly one millimeter, which led to their being termed as carbon nanotubes or CNTs. The nanotubes produced were multi walled nanotubes (MWNTs) i.e. they had many capped concentric walls of different diameters ranging from 2-15 nm for inner diameter to 2-30 nm for outer diameter with tube lengths several µm long.

In 1993, Iijima and Ichihashi [4] reported synthesis of single wall nanotubes (SWNTs) with diameters of 1-2 nm and length of 30-40 nm. Later, in 1996, Smalley reported a method for producing SWNTs with uniform diameters and structures with high yield by laser vaporization of graphite. Generally, the number of defects observed in SWNTs was comparatively lower than the defects observed in MWNTs.

Based on the arrangement of the hexagons around the circumference of the nanotube, there are three structural sub-categories, all shown in Fig. 1.2. The first of
these nanotube structures is termed *armchair* because the carbon atoms link together in the shape of an armchair. The second category is named *zig-zag* because the hexagonal rings of carbon are in a straight line as the carbon tube circumference is unwrapped. The third form is termed *chiral* indicating that the hexagonal carbon rings spiral in either direction along the circumference. This third structure is believed to be the most commonly occurring structure for nanotubes.

Carbon nanotubes have many unique properties which make them useful for a range of applications. For example, nanotubes can be either electrically conductive or semiconductive, depending on the degree of twist of the tubes, leading to their possible use in applications in nanoscale wires and electrical components. They exhibit electrical conductivity as high as metals like copper. Their thermal conductivity is comparable to that of diamond and their strength is 100 times greater than that of steel at one sixth the
weight. The Young's modulus of SWNTs is over 1 Tera pascal and the estimated tensile strength is around 100 Giga Pascal. These mechanical properties make them ideal for use in reinforced composites and nanoelectromechanical systems (NEMS).

In addition to these, many other potential applications have been proposed for carbon nanotubes, including hydrogen storage and energy conversion devices, sensors, field emission displays and radiation sources, nanometer-sized semiconductor devices, atomic force microscopy (AFM) probes and future applications in computers.

1.2 Research Goals and Thesis Overview

The goals of the research presented in this thesis are:

(1) To determine processing parameters for growth of carbon fibers and CNTs using cyclohexane as a carbon source and Cu-Ni alloy as catalyst layer.

(2) To estimate the optimum Cu-Ni catalyst thickness for CNT growth and examine the effect of annealing.

(3) To examine the grown layers.

Chapter 2 gives a brief introduction to the three main methods of synthesizing nanotubes and talks about the two primary mechanisms, namely the base growth and the tip growth mechanisms observed to-date in formation of nanotubes. In chapter 3, a review of contemporary papers dealing in thermal CVD and some papers detailing the results from plasma CVD is given. Chapter 4 details the process flow used in this research, methodology for substrate preparation with catalyst and the experimental setup for carbon CVD film growth. Chapter 5 gives the results of the SEM analysis done on the carbon films produced from different processing conditions and sheet resistance.
measurements on those samples. Chapter 6 provides summary, conclusions and gives direction for future research.
2. BACKGROUND THEORY AND MECHANISMS FOR CNT DEPOSITION

There are three main methods to synthesize aligned and non aligned CNTs. A brief review of these processes used to synthesize both single and multi wall carbon nanotubes are described in this chapter.

2.1 Laser Ablation

Laser ablation or evaporation was first used by Smalley’s group in 1985 in the production of C_{60} and later in 1995 to produce CNTs. The setup used is shown in Fig. 2.1. This uses a laser to evaporate the carbon from a graphite target heated at 1200 °C in a furnace in a 500 Torr helium or argon gas ambient. The argon gas carries the vaporized carbon and deposits it on the tip of a copper collector which is water cooled. If pure graphite targets are used, multi wall nanotubes (MWNTs) are observed among the

Fig. 2.1 Setup for laser ablation. After reference [6].
fullerene deposits on the collector. When doping is performed on the target with nickel, iron or other transition metals, single wall nanotubes (SWNTs) are collected. These metals are mixed in a very small percentage, around 0.5 percent by weight. The SWNTs produced may retain nanoparticles of metal inside them and may need to be purified after growth. The yield of the nanotubes produced by this process is 0.4 gm/hr and approximately 70% of the deposit on the copper collector had rope like clustered SWNTs of 10-20 nm diameter and 100 µm in length. High quality SWNTs can be produced by this method.

2.2 Arc Discharge

Initially, the arc discharge process was used by Iijima to produce CNTs. It is still considered a cheap and easy method for producing large quantities of nanotubes. The setup for this is shown in Fig. 2.2.

![Fig. 2.2 Setup for arc discharge. After reference [7].](image-url)
This involves use of two graphite rods of 6-9 mm diameter used as anode and cathode separated by about 1 mm in a reaction chamber which is filled with an inert gas like argon at a pressure of 500 Torr. A low voltage of 20-40 V and current of 50-100 A is applied between the electrodes producing a discharge. Electrons from the discharge strike the anode causing graphite material to come off from the anode, indicated by the arrows in Fig. 2.2. Cathode is water cooled so the clusters emanating from the anode can condense in different forms like amorphous carbon, buckyballs and nanoparticles. Similar to laser ablation, MWNTs of 10-20 nm are observed in the deposits when pure graphite rods are used and SWNTs of diameters 1-2 nm can be found in the core region of the deposits when the anode is doped with metals like nickel, iron and cobalt. The quality of the CNTs is controlled by the current and the pressure of the inert gas used.

2.3 Chemical Vapor Deposition

The most recent technique which has come into the forefront of growth for nanotubes is the chemical vapor deposition (CVD). This process was first performed by the Xie group [8] from the Chinese Academy of Science in Beijing in 1996 to produce a highly vertical aligned nanotube film 50 µm thick. This method has grown to become one of the most efficient, easy and widely used technique to produce nanotubes wherein the tube length, alignment and diameter can be controlled by the growth parameters such as temperature, pressure, type of the gas ambient and catalyst used in the CVD process. The deposition can be done on patterned catalysts or on large areas. Another advantage is that only nanotubes can be produced without simultaneous deposition of other forms of carbon obtained in the other two processes. Different types of CVD used for CNT deposition include thermal, plasma, atmospheric pressure, low pressure and metal organic
chemical vapor deposition. Of these, the thermal and the plasma CVD are the ones most commonly used methods for CNT deposition.

2.3.1 Thermal CVD

This particular method of CVD is the most simple and the most widely used method for large scale production of CNTs. The setup for thermal CVD is shown in Fig. 2.3. First process in CVD layer deposition is the substrate preparation. Silicon, silicon oxide or glass is usually employed as a substrate. The substrate is usually coated with a catalyst metal like iron, nickel or cobalt. This catalytic layer is deposited by electron beam, thermal evaporation or sputtering. The catalyst film is then patterned so that it remains only at predetermined locations. This allows nanotubes to grow only where the catalyst is present, giving the advantage of selective growth possibility by the CVD technique. Substrates with patterned catalyst on them are placed on the quartz boat and

Fig. 2.3 Thermal CVD setup.
are usually heated between 550 and 850 °C. One important requirement between the catalyst deposition and the start of the CVD growth is to obtain nucleation of catalyst particles on the catalytic surface layer. This can be achieved by thermal annealing in hydrogen or ammonia and/or by using a wet etch in an etchant like dilute hydrofluoric acid (HF). The smooth metal film splits into metal particles and islands during this annealing process, forming nucleation sites for the hydrocarbon molecules, which after depositing on these particles will continue to grow to form carbon structures. The basic decomposition reaction during CVD is splitting of the hydrocarbon such as methane (CH₄), ethane (C₂H₆) or acetylene (C₂H₂) molecules into carbon and hydrogen atoms due to high temperature.

\[ C_xH_y \rightarrow xC + nH_2 \]  where \((x, y, n) = (1, 4, 2)\) or \((2, 6, 3)\) or \((2, 2, 1)\) etc.

In most reported cases, hydrogen is made to flow during the CVD process. The main role of hydrogen is to reduce the catalyst which might otherwise oxidize in its absence. Also, the rate at which the hydrocarbon decomposes is reduced by this hydrogen. This prevents passivation of the catalyst surface caused by excess deposition of carbon from the vapor phase. This avoids deposition of amorphous carbon and enhances growth of carbon filaments or nanotubes.

Some of the commonly used carbon precursors are methane, acetylene and carbon monoxide. After CVD is performed for a period of time, the precursor supply is cut off and the furnace heaters are switched off. The samples with the deposited carbon films are removed after the tube cools down to room temperature. Thermal CVD has been performed in this manner to grow uniform films of CNTs. Well aligned nanotubes are obtained once the density of the growing nanotubes reaches a certain limit. At this point,
they stop growing in the lateral direction because of the obstruction from the adjacent structures, and are forced to grow in the vertical direction. This effect is called the crowding effect [9] and long MWNTs 50-120 nm in diameter with a length of 130 µm have been observed. However, this kind of alignment of the NTs from the thermal CVD method is difficult to achieve in most cases [10].

2.3.2 Plasma CVD

In this case, instead of using temperature, plasma is used to activate the reaction rates of the precursors. Glow discharge in the chamber is generated by voltage applied to both electrodes. Due to this, the temperature needed for deposition of nanotube films is lowered compared to temperatures required for the thermal CVD case. This is referred to as plasma or plasma enhanced CVD (PECVD) and is shown in Fig. 2.4. It can be used

Fig 2.4 Plasma CVD setup. After reference [11].
for growing CNTs on soda lime glass at substrate temperature less than 550 °C. The latter is the melting point for glass. This is a good method to produce both well aligned dense NTs and free standing MWNTs.

Either a DC, RF or microwave plasma can be employed. The lower electrode which is grounded is the one on which the substrate is placed. The flow of the hydrocarbon along with etchant gas species like ammonia or hydrogen for particle nucleation is controlled and is supplied from an inlet over the top electrode.

For high frequency power, RF (13.56 MHz) or microwave (2.47 GHz) power can be chosen to create the plasma. An electric discharge is generated in the chamber between the two electrodes. A rotating susceptor acts as the substrate holder and has embedded heating coils to heat the substrate at a steady temperature. The entire setup is placed in a quartz tube and a vacuum pump is used to maintain required low pressure. Once the metal nucleating particles form on the catalyst layer, the hydrocarbon species is allowed to flow in. Nanotubes start to grow from the nucleated metal particles with the carbon atoms depositing from the glow discharge. Highly aligned nanotubes are seen when neighboring structures start to come together by Van der waals force and in this case result in 100-120 nm diameter nanotubes.

2.4 Growth Mechanisms

2.4.1 Base and Tip Growth Mechanisms

More than one mechanism of growth can result in growth of nanotubes. The exact method by which nanotubes grow has not been determined with certainty yet. However most of the cases in literature where carbon nanotubes have been synthesized follow one of two main mechanisms, namely the base (or root) growth and the tip growth
mechanism. These two mechanisms are shown in Fig. 2.5(a) and (b) respectively. Initially, when the catalyst (nickel, cobalt or a compound) is annealed in argon/hydrogen, ammonia or when etching is performed in HF, the smooth film is etched to form egg shaped particles of catalyst 100-400 nm in diameter.

![Diagram of growth mechanisms](image)

Fig. 2.5 (a) Root and (b) Tip growth mechanisms. After reference [12].

These particles now act as the sites for commencing the nanotubes growth. As the time of dipping in HF is increased, the size of the Ni particles produced decreases. This can lead to higher nanotube density. For the same HF dipping time or ammonia treatment, the diameter of the catalyst particles produced increases with the thickness of catalyst film [13,14].

In the root growth mechanism in Fig. 2.5(a), the catalyst particle remains at the bottom of the nanotube. When the hydrocarbon passes over the catalyst particle, the
carbon molecules diffuse into the particles through the edges and saturate it. At this stage, graphitization occurs and sheets of graphite start to form on top of the particle. These sheets are closed at the top. This leads to multiple walls of carbon with the catalyst particle remaining at the base of the nanotube and attached to the substrate.

For tip growth as shown in Fig. 2.5(b), the polycrystalline catalyst islands formed act as nucleation seeds for the carbon growth to start from. At low temperatures, the sizes of the particles are small and the atoms of carbon decompose and then dissolve in the catalyst particle, initiating the growth process. When saturation of the nickel is reached, because of the further diffusion of carbon, growth continues by successively depositing the carbon molecules below the catalyst particle, forming multiple sheets of graphite. This pushes the catalyst particle upward where it stays at the tips of the nanotubes grown. However, in both tip and base growth cases, the carbon atoms do not diffuse through the center of the particle, leaving a hollow core in the center. If the size of the catalyst particle is small (2-3 nm), SWNTs are produced and when the sizes are larger, MWNT are grown. At higher temperatures, growth is more likely to take place on larger catalyst particles leading to formation of MWNTs with larger diameters.

The grown CNTs are usually characterized by scanning electron microscopy and high resolution transmission electron microscopy (HRTEM). SEM is performed to observe the length, diameter and the alignment of the nanotubes. HRTEM is done to observe the number and the structure of the walls of the nanotubes produced.
3. SELECTED REVIEW OF CVD GROWN CNTS

Choosing the right precursor and catalyst for growth of CNTs in this research makes it imperative to know the precursors, catalysts and the process conditions used by other groups previously to synthesize randomly oriented and vertically aligned nanotubes. This chapter discusses selected papers where CNTs have been produced by thermal and plasma CVD techniques.

Ducati et al. [15] have reported growth of nanotubes at 550 °C, 700 °C and 850 °C with acetylene hydrocarbon. A 3 nm thick nickel film deposited on a 50 nm thick silicon oxide layer is employed as catalyst in their work. They have used ammonia gas to anneal the catalyst films to produce the metal particles. Specifically, the samples are heated to 700 °C for 15 min at a pressure of 3 Torr in ammonia ambient. The operating pressure at which CVD is performed is 4 Torr and the process time for all runs is 15 min. The MWNTs which are obtained from this thermal CVD are spaghetti-like and randomly oriented. It is seen that the diameter of the nanotubes grown increases from 15 nm at 550 °C to 75 nm at 850 °C, as shown in Figs. 3.1 a) - c). For the same range of temperatures, plasma CVD at 600 V is performed using acetylene. In contrast to thermal CVD, plasma CVD results in vertically aligned MWNTs with outer diameters ranging from 30 nm at 550 °C to 100 nm at 850 °C as shown in Figs. 3.1 d)-f).

SEM analysis indicated that the catalyst particles are observed at the tips of the nanotubes for both thermal and plasma CVD indicating that tip growth mechanism is taking place in both these cases. For thermal CVD, at 550 °C, the diameter of the nickel particles is observed to be 5 nm and is almost equal to the inner diameter of the tubes.
The diameter of nickel particles increases to 75 nm which is approximately equal to the outer diameter of the tubes at 850 °C. In the case of plasma CVD, the nickel particle size increases from 30 nm at 550 °C to 100 nm at 850 °C.

In addition to single elements like nickel, alloys like cobalt-nickel have been used by Lee et al. [16] as catalysts in thermal CVD to obtain well aligned nanotubes. A 100 nm thick Co-Ni film is evaporated on 300 nm silicon oxide samples. Nucleation is performed by dipping the samples for 150 sec in diluted HF solution and then placing the samples in the CVD reactor. The samples are also subjected to treatment in ammonia at a rate of 120 sccm for 20 min at 950 °C before acetylene (C₂H₂) is allowed to pass through the chamber for 10-20 min. Vertically aligned MWNTs 130 µm in length and diameters varying from 50 to 120 nm are obtained. The SEM images of the aligned NTs are seen in
The magnified view of the nanotubes is seen in Fig. 3.2(b) and the top view of the NTs is seen in Fig. 3.2(c). The alignment was due to the crowding effect discussed previously wherein the nanotubes are forced to grow in only the vertical direction due to the obstruction in the lateral direction from the high density of the nanotubes in the surrounding area.

An alloy of copper and nickel has been used by Jong et al. [17] as a catalyst for PECVD. The effect of different ratios of copper and nickel on the structure of the nanotubes is examined. Initially, the metal salts, nickel acetate tetra hydrate and copper chloride are mixed in a stirrer, spin coated on silicon wafers and then dried at 600 °C for 30 min in a furnace to get a solid catalyst film. These samples are place in a microwave PECVD system where a power of 1100 W and DC bias of 350 V is applied under a pressure of 30 Torr. Hydrogen is used to anneal the films. Methane with a flow rate of 0.5 sccm is then introduced and CVD is carried out at 900 °C. The results of CVD with different Cu-Ni ratios are shown in Fig. 3.3. Initially, when the catalyst composition is
pure nickel, 50 nm diameter carbon tubules are formed in Fig. 3.3(a). When the composition is 20% Cu-80% Ni as seen in Fig. 3.3(b), these tubules are still seen, indicating that the addition of copper has not had a significant effect on the morphology of the nanotubes. When the composition changes to 40% Cu-60% Ni, as seen in Fig. 3.3(c), due to relatively high percentage of copper, carbon stops depositing on areas where copper atoms tend to cluster. This limits the regions on the catalyst film where diffusion can take place. Carbon filaments or fibers start to form at this point. However, these fibers have defects due to the limited areas of adsorption of carbon and are twisted to
reduce these defects. Result for 60% Cu-40% Ni composition is shown in Fig. 3.3(d) where carbon begins to deposit on these twisted filaments and is able to form straight filaments on top of the twisted structures. Further increase of copper to 80% Cu-20% Ni as seen in Fig. 3.3(e), gives even more twisted filaments which now begin to show marked spiral shapes. Only copper, when used as the catalyst is not seen to yield any nanotube growth. The tubules and filaments formed in their process have diameters between 50 nm and 200 nm.

It has been noticed that single wall nanotubes are usually grown at higher temperatures than multi wall nanotubes. This has been noted by Cui et al. [18] where they use a multilayered catalyst film for thermal CVD. Thin films of aluminum, iron and molybdenum with thicknesses of 10 nm, 1 nm and 0.2 nm respectively were successively deposited by electron beam evaporation on silicon substrates followed by growth from 2 sccm acetylene for 20 min at temperatures between 600 °C and 1100 °C in steps of 100 °C. Aluminum is chosen as one of the catalysts as it is found to be favorable for the growth of SWNTs. An argon and hydrogen mixture is first used to anneal the catalyst film for 1 hour at the growth temperature in each case before CVD is performed. The results of CNT growth at different temperatures are seen in Figs. 3.4 a)-f). Vertically aligned MWNTs with an average length of 1 µm and diameter of 20-30 nm are seen at 600 °C in Fig. 3.4(a). However, TEM analysis revealed that the grown CNTs are defective. When the temperature is raised to 700 °C, a sudden increase in height to 54 µm along with simultaneous decrease in the amount of defects at the wall is observed and shown in Fig. 3.4(b), suggesting it to be an optimum temperature for growth of low defect vertically aligned MWNTs due to the crowding effect. On a further
temperature increment to 800 °C, as seen in Fig. 3.4(c) the vertical alignment is lost. However, due to decrease in the density of the NTs, bundles of SWNTs with length of 10 µm start to appear. At 900 °C, both randomly oriented SWNTs with diameters of 1-2 nm and CNT bundles are seen together in Fig. 3.4(d), making it optimum for the growth of SWNTs. TEM analysis of the growth at 1000 °C in Fig. 3.4(e) showed that random nanotubes and fibers with a highly defective nature started to appear. At 1100 °C, only amorphous carbon deposits are seen in Fig. 3.4 (f).

Kim et al. [19] have synthesized nanotubes on 200 nm nickel thin film catalyst coated on soda-lime glass. First, a 5 µm thick silver films is coated by screen printing on soda-lime glass substrate. The next step is to electroplate nickel by using nickel sulphate, ammonium chloride and boric acid solution and then pattern it. Separately, a 100 nm

Fig. 3.4 Cross sectional images of CNTs grown at (a) 600 °C (b) 700 °C, (c) 800 °C (d) 900 °C (e) 1000 °C and (f) 1100 °C. From reference [18] with permission (Appendix: A5).
palladium film is evaporated on an alumina substrate. The two substrates are loaded in a quartz tube facing each other and separated by 5 mm with the nickel coated substrate facing downward and the palladium coated substrate facing upward. The palladium acts as a co-catalyst and lowers the deposition temperature of nanotubes to 550 \(^0\text{C}\). Ammonia is first supplied at 100 sccm for 20 min at 550 \(^0\text{C}\) to anneal and etch the Ni film into particles. Growth is carried out using acetylene at 20 sccm for 10 min. After the thermal CVD process is complete, the tube is cooled down by flowing argon till it reaches room temperature. Vertically aligned CNTs 100-200 nm in diameter and curled nanotubes 30-40 nm in diameter are shown in Fig. 3.5. Raman spectroscopy reveals that the nanotubes have multi walled structure with some defective sheets.

Lee et al. [20] have also grown carbon fibers and graphite whiskers using the same setup and investigated the importance of using palladium as co-catalyst. In this case, they have used a cobalt-nickel catalyst on 300 nm oxidized silicon wafers. The thickness of the catalyst deposited is 100 nm which is then surface treated by dipping in diluted HF for 200 sec. The 100 nm thick palladium (Pd) is separately deposited on another oxide wafer. They are then loaded in a tube and separated by 3 mm with the Co-Ni substrate facing downward and the Pd coated substrate facing upward. After treatment by ammonia at 80 sccm for 10 min at 850 \(^0\text{C}\), the growth was carried out using acetylene for 10 min at 550 \(^0\text{C}\). SEM pictures indicate that spaghetti-like CNTs, 60-80 nm in diameter are grown on the Co-Ni coated substrate, as shown in Fig. 3.6(a).
With chromium as co-catalyst instead of Pd, only carbon fibers are seen at the same growth temperature as in Fig. 3.6(b). When platinum is used instead of Pd, only some graphite whiskers with 100-200 nm diameters are seen in Fig. 3.6(c). These results show that palladium plays a crucial role in the formation of CNTs in this process. In addition to commonly used precursors like acetylene and methane, a catalyst/precursor mixture often used in literature is ferrocene and xylene. The boiling point for xylene is 140 °C while the decomposition temperature of ferrocene is 190 °C. Andrews et al. [21] detail a method for bulk production of MWNTs using this mixture. Ferrocene is dissolved in xylene first to get a solution with 0.75 atomic % (Fe/C ratio). This is fed by a syringe pump into a preheater zone heated to 175 °C in the CVD reactor.
The carrier gas used is a 90% argon-10% hydrogen mixture, which carries the heated vapors from the preheater into the furnace. Quartz substrates are loaded into the reactor to collect the nanotubes and it was noticed that at a process temperature of 675 °C and an operating pressure of 760 Torr, vertically aligned MWNTs with diameters 20-25 nm have been synthesized. The Fe particles in this case have been noticed at the tips of the structures indicating tip growth mechanism.

Nureshev et al. [22] have used Fe(CO)₅ taken in a bubbler as the source for metal particles, methane as the precursor, a carrier gas like argon and hydrogen gas as the reducing agent. The carrier gas is introduced into a bubbler filled with Fe(CO)₅ and carries the gas into the tube heated to 200 °C for 30 min, through a water cooled injector
which reduces the probability of formation of the iron particles before it reaches the samples placed inside. Fe(CO)$_5$ decomposes due to the high temperature and deposits a layer of iron on the substrate. After this is complete, the supply of Fe(CO)$_5$ is shut off and CVD is performed using 500 sccm argon and 100 sccm of hydrogen to carry methane at 13 sccm for 15 min at a much higher temperature of 1100 $^\circ$C. The advantage in using methane is that it shows a low rate of formation of CVD products from self pyrolysis. A layer of non aligned MWNTs 20 nm in diameter and 2-3 µm in length grown in absence of hydrogen for 1 min is seen under SEM analysis in Fig. 3.7(a). The effect of hydrogen during CVD has been investigated by carrying out CVD using only argon. The carbon tubes which are formed during annealing using only argon are much larger in size than which are produced using both argon and hydrogen. CNTs, 35 nm in diameter were seen in 3.7(b) for no hydrogen for a process time of 5 min. Carbon fibers, 5.5 µm in diameter are observed after CVD in the absence of hydrogen for a long deposition time of 20 min as shown in Fig. 3.7(c) and Fig. 3.7(d). These results indicate the necessity of hydrogen for reducing the size of the metal particles and also reducing the diameter of the CNTs grown. Thus, if only argon is used, deposition due to excess decomposition of methane will dominate and will only produce carbon fibers and carbon rods.

Morjan et al. [23] have also used an annealing mixture of argon and hydrogen for 0.5-20 nm deposited Fe films at an annealing temperature of 750 $^\circ$C for 15 min. The flow rate for argon was set at 600 sccm, hydrogen was set at 100 sccm while acetylene was set at 10 sccm. It is seen that the particle diameter increases with increasing film thickness from 26 nm for a 0.5 nm Fe thin film and reaches 475 nm for a film thickness of 20 nm.
It is observed that here, nanotubes do not grow if the diameter of the particles exceeds 100 nm. Pure MWNTs are only produced from small particles. The only kind of deposits which will be seen for large particles will be amorphous carbon due to self pyrolysis of acetylene.

Yoon et al. [24] have performed thermal CVD growth by using acetylene as the carbon source and compared nickel and cobalt as catalysts on silicon oxide substrates to see which gave better growth. Sputtered catalysts used are 2-10 nm in thickness. They are annealed in argon and hydrogen at 800 °C. In the case of cobalt, after annealing, particles 20-30 nm in diameter are seen to be uniformly distributed on the surface. For nickel, however, particles with varying diameters from 20-60 nm are observed. After the
annealing is complete, growth is carried out at a pressure of 2 Torr in acetylene for 1 hour at 800 °C. The nanotubes from the cobalt particles, as expected, are 20-30 nm in diameter and 13 µm in length. The CNTs are vertically aligned because of high density due to the closely spaced uniform particle size. The nanotubes from nickel, on the other hand, are randomly oriented on the substrate. SEM pictures for both cases, Co and Ni are shown in Fig. 3.8(a) and Fig. 3.8(b) respectively. It is also seen that nanotubes did not grow from particles which are more than 50 nm in diameter, the only deposition in this case being amorphous carbon and carbon fibers. In both cases, metal particles are seen at the tips of the nanotubes.

![SEM images of the CNTS on (a) Co (b) Ni as catalyst. From reference [24] with permission (Appendix: A7).](image)

Fig. 3.8 SEM images of the CNTS on (a) Co (b) Ni as catalyst. From reference [24] with permission (Appendix: A7).
Jung et al. [25] have investigated the use of ammonia for producing metal catalyst particles and acetylene for the growth of aligned nanotubes. The thickness of the nickel or cobalt films sputtered in their case was 3 nm which is then annealed using hydrogen at 1 Torr in a rapid thermal process furnace for 15 min at 800 °C. For both nickel and cobalt, 17-58 nm diameter particles were formed. However, they observed more uniform distribution for cobalt compared to nickel. These samples are then put in a loading system connected to the furnace and treated in hydrogen at 200 sccm or ammonia at 100 sccm. After this is complete, the samples are then loaded into a furnace already heated to 950 °C. The volume of the acetylene added for the deposition to the gas flow is varied from 2.4 to 16.7 % by vol. for CVD growth. When only hydrogen is used, the growth on nickel particles in 2.4 vol. % of acetylene is shown in Fig. 3.9(a). The growth is scattered and shows a very low number of randomly oriented carbon filaments due to passivation of the Ni film by amorphous deposits of carbon and deposited tube diameters are around 22 nm. In case of cobalt shown in Fig. 3.9(b) for the same volume fraction of acetylene, the growth is better with a higher density of CNTs observed due to the Co film not being passivated. This shows that the structure of the NTs formed depends on the type of catalyst. When ammonia is used instead of hydrogen, the production is improved drastically for Co and Ni as shown in Figs. 3.9(c) and 3.9(d). The growth for both cases shows vertically aligned nanotubes. For the case of 16.7 vol. % of C\textsubscript{2}H\textsubscript{2}, the NT growth rate is 1.6 µm/min for Ni and 2.3 µm/min for Co. This is seen even when the volume of the acetylene is increased leading to a higher rate of supply of carbon indicating that the use of ammonia avoided the catalyst films getting passivated. This is probably due to the
Fig. 3.9 SEM images of (a) growth in 2.4 vol. % of C₂H₂ on Ni using H₂ (b) growth in 2.4 vol. % of C₂H₂ on Co using H₂ (c) growth in 16.7 vol. % of C₂H₂ on Ni using NH₃ (d) growth in 16.7 vol. % of C₂H₂ on Co using NH₃. From reference [25] with permission (Appendix: A8).

nitrogen from the ammonia forming a nitrogen layer on the nickel and cobalt catalyst surfaces which is required for CNT growth.

Lee et al. [26] have also reported bamboo-like MWNTs grown from acetylene using a 100 nm thick nickel film. The 300 nm silicon oxide samples on which the Ni films are deposited are dipped in a dilute HF solution for slightly more than 3 min and then treated by NH₃ with a flow rate of 50-200 sccm for 20 min at 950 °C for further particle nucleation. Growth is performed by thermal CVD from C₂H₂ (acetylene) at 60 sccm for 15 min. Nanotubes obtained are 60 nm in diameter and 50 µm in length and are vertically aligned. TEM analysis is performed after removing the nanotubes from the substrate in acetone using an ultrasonic bath. TEM picture indicates that the CNTs are hollow, closed at the top and have compartments spaced 100 nm apart. The inner
diameter of the NTs is 20 nm and the outer diameter is 60 nm. All the compartments are curved towards the tip. The CNTs show a base growth mechanism with the nickel particles staying at the bottom of the tubes. The thickness of the CNTs increases due to the interconnection of the compartment layers.

Lee et al. [27] have reported growth of bamboo-like MWNTs using a 100 nm thick Fe film. The oxide samples are pretreated by the same method in HF and ammonia. Growth is performed by thermal CVD from C\textsubscript{2}H\textsubscript{2} at 60 sccm for 10 min at temperatures ranging from 600 °C to 950 °C. The diameter of the MWNTs is seen to increase from 20 nm at 600 °C to 300 nm at 950 °C. However, at all these temperatures, the nanotubes are vertically aligned to the substrate. At 600 °C, Fe particles are noticed at the base of the nanotubes. At higher temperatures, these particles are not seen at the base or at the tips. This is probably due to melting of the Fe particles at the higher temperatures.

In another study, Lee et al. [28] have also reported on the effect of the dipping time in HF solution on the structures grown during CVD. Here, 100 nm Ni or Co film evaporated on 300 nm oxidized Si wafers are dipped for 200 and 300 sec in dilute HF (HF:de-ionized water=1:16) followed by CVD in acetylene at 15 sccm for 20 min at 850 °C. In the case where the samples have been dipped for 300 sec, noodle shaped nanotubes 200 nm in diameter are seen lying on the substrate as shown in Fig. 3.10(a). Metal particles are observed at the tips of the nanotubes. In the case where the samples have been dipped for 200 sec, carbonaceous deposits are seen after CVD as shown in Fig. 3.10(b). This is due to the insufficient HF etching time for proper nucleation. As the particles are not formed properly, the deposits on the catalyst surface hence, are in the form of amorphous carbon.
Qingwen *et al.* [29] have investigated different hydrocarbons like benzene, cyclohexane and hexane as carbon sources. The catalyst used in their case is a MgO and Fe alloy. This particular catalyst is chosen as it is suited for growth of both MWNTs and SWNTs. For preparing the catalyst, 1 gram of MgCO$_3$ is added to iron nitrate solution (10 mg/ml) and heated to 105 °C to get a solid mixture. This powder is put in an alumina boat and loaded into a furnace. The temperature in the furnace is then increased to 850 °C while introducing argon at 300 sccm. After the temperature is stabilized, the hydrocarbon is carried into the chamber and the CVD process is carried out for 30 min. After the tube has cooled down to room temperature, the catalyst is removed by using HCl solution leaving only the CNTs which can be characterized.

![SEM pictures of growth on Co coated oxidized Si substrate dipped in HF for (a) 300 sec (b) 200 sec. From reference [28] with permission (Appendix: A3).](image)

Fig. 3.10 SEM pictures of growth on Co coated oxidized Si substrate dipped in HF for (a) 300 sec (b) 200 sec. From reference [28] with permission (Appendix: A3).
When benzene is used as the precursor, SWNTs with diameters of 1 nm were produced. In the case of cyclohexane, MWNTs 20-30 nm in diameter are seen. However, when hexane was used, the deposits seen are mostly amorphous flakes which contain a few MWNTs. This shows that the type of deposit obtained also depends on the structure of the hydrocarbon used.

In this chapter, papers detailing the use of different precursors like methane, acetylene, xylene, benzene, hexane and cyclohexane for thermal CVD have been discussed. The use of elements like Ni, Co, Pd, Cr, Pt, Fe along with alloys like Co-Ni, Cu-Ni and liquids such as ferrocene as catalysts are discussed. Carbon fibers and SWNTs have been observed in papers by Cui et al. [18] and Lee et al. [20] in addition to the MWNTs produced. The MWNTs observed are either vertically aligned or randomly oriented on the substrate depending on the process conditions. Effect of using argon, argon-hydrogen and ammonia during annealing and CVD growth on the diameter and length of the CNTs grown in the work done by Jung et al. [25] and Nureschev et al. [22] has been discussed. It indicates that the use of hydrogen is essential to produce small diameter nanotubes.
4. EXPERIMENTAL SETUP

In the previous chapter, it was seen that Jong et al. [17] reported the growth of 50 nm diameter tubules with the catalyst composition being 20% Cu-80% Ni. This particular alloy is chosen as the catalyst in this present work in order to produce small diameter carbon tubules. Also, cyclohexane has been one of the precursors used by Qingwen et al. [29] where MWNTs with 20 nm to 30 nm are produced. This hydrocarbon is chosen as the carbon source for the CVD in this work, as not much research has been done on this particular source of carbon to-date. This hydrocarbon and catalyst combination also has not been used previously to produce either randomly oriented or vertically aligned CNTs. This chapter gives the details of patterning the Si and SiO₂ substrates with photoresist followed by catalyst deposition. These Cu-Ni films are then used as a catalytic layer in the CVD process. The procedure for performing the CVD is described.

4.1 Experiment

In this work, 4” diameter (100) oriented, p-type, 5 to 10 Ω-cm resistivity silicon and silicon oxide coated Si wafers, with a thickness of 475-575 µm have been utilized. In the case of the oxidized Si wafers, the thickness of the oxide is 1 µm. A critical step before the CVD process is deposition and patterning of the catalyst. In this case, 20% copper-80% nickel has been utilized as a catalyst. The purpose here is to produce tubule-shaped nanotubes which can be used for field emission applications.

Before any processing is done, the samples must be cleaned. A pyrex dish is filled with acetone. The dish is then heated to 50 °C on a hot plate. Once the solution is warm,
the substrate wafers with or without oxide on top are placed in the bath for 10-12 min. This removes oil, organic residues and particles upto 0.5 µm in size from the surface. The samples are placed in a dish of deionized (DI) water for 2-3 min. The samples are then removed and placed in a dish of methanol for 5 min and gently agitated. After this, the samples are blown dried in nitrogen. The substrate preparation for silicon wafers prior to deposition is described below in Fig. 4.1 which consists of the following steps: 1) spin coating of photoresist 2) exposing and developing photoresist 3) sputtering of catalyst (Cu-Ni) and 4) photoresist stripping and lift-off.

Fig. 4.1 Process flow for CVD growth on Si substrate.
The wafer is now ready for CVD growth. The substrate preparation for oxidized wafers will be discussed later in this chapter.

4.1.1 Spin Coating of Photoresist

The silicon samples are spin-coated with positive S1813 photoresist (PR). The spin cycle for S1813 is shown in Fig. 4.2. The resultant PR thickness after this spin cycle is 1.1 µm as measured by an Alpha-step 200 thickness profiler. The wafers with resist are then soft baked at 100°C for 25 min in an oven.

![Spin cycle for photoresist S1813](image)

Fig. 4.2 Spin cycle for photoresist S1813.
4.1.2 Exposing and Developing of S1813 PR

The samples are removed from the oven after soft baking cycle. The wafer is exposed under broadband ultraviolet (UV) light in a Q4000 Quintel two-sided contact aligner. The 1 µm thick PR is exposed for 16-17 sec. The mask design used during lithography is shown in Fig. 4.3. Same mask is used for both silicon and the silicon oxide-coated wafers. The mask pattern consists of alternating dark and transparent strips 1.3 cm wide and 10.5 cm long.

Fig. 4.3 Mask used for patterning on both Si and SiO₂ coated substrates.
The PR below the dark areas on the mask remains after the developing step. Upon exposure, the samples are dipped for 10-15 sec in a petri dish with MF 354 developer. After the patterns have been fully delineated, the wafer is removed from the dish and DI water is used to remove traces of the developer.

4.1.3 Sputtering of Cu-Ni

Catalyst layer is next sputtered on the wafers having PR patterns. A magnetron sputtering system, E306A from Edwards is used here. This technology uses magnets to confine the glow discharge plasma to the region closest to the target plate. This improves the deposition rate by maintaining a higher density of ions, making the electron/gas molecule collision process more efficient. The pre-deposition sputtering pressure is maintained at \(9.0 \times 10^{-6}\) Torr. The sputtering target is an alloy of 20 % copper-80 % nickel. RF magnetron sputtering is used here as DC sputtering is likely to be unstable. Generally, magnetic targets like nickel, iron and nickel-copper are difficult to sputter as the reflected RF power does not go to zero. The reflected power is a result of mismatching the power supply impedance with the reaction chamber impedance and this level should always be kept at a minimum.

In the case of Cu-Ni target, the reflected power can be reduced to a minimum of 1-2 W by increasing the operating pressure to 3-4 \(\times 10^{-2}\) Torr instead of the value of 1 \(\times 10^{-2}\) Torr used for sputtering copper and other non magnetic materials. The RF power used is 200 W during all sputtering runs in this work. In order to obtain the Cu-Ni alloy sputtering rate, each wafer is covered with an aluminum foil to form a step and sputtering is carried out for 45 min on three wafers simultaneously. The film-substrate step is measured with a Tencor alpha step 200 to obtain the step height of the deposited films.
The average thickness of the sputtered films on the three samples is determined to be 1093.5 nm which gives a rate of 24.3 nm/min. The thinnest film used for the experiments in this research is nominally 2-3 nm in thickness and the thickest film used is nominally 150 nm in thickness. For these extreme cases, the sputtering times are 5 sec and 370 sec respectively. XPS results on sputtered Cu-Ni films of different thicknesses indicated that the film compositions are nominally 20.9% Ni-79.1% Cu in all cases indicating uniform sputtering rate of the two metals from the alloy target.

4.1.4 Photoresist Stripping and Lift-off

After the catalyst films are deposited on the entire surface of the sample, the areas where Cu-Ni is not desired are removed by lift-off technique while stripping the underlying photoresist. This is done by immersing the wafer in a dish containing acetone for about 1 min. The PR patterns along with the copper-nickel layer on top are removed leaving only the catalyst in long patterns on the Si wafers.

4.2 Oxidized Silicon Substrates

In case of oxide-coated Si wafers, the process flow is shown in Fig. 4.4. The initial step of spin coating and soft baking approximately one micron thick PR is the same as for Si substrates except that in this case, the PR coats the oxide instead of silicon. The exposure and developing steps are also the same as before. Here, developed PR is used as mask for selective etching of the oxide layer in a buffered oxide etch (BOE) where isotropic etching i.e. etching in all directions at the same rate takes place. The BOE solution consists of NH₄F, HF and deionized (DI) water.

The etch rate of oxide in BOE is in the range of 90-120 nm/min. It takes approximately 11 min to etch the 1100 nm thick oxide. Patterned wafer with oxide under
the resist is placed in a plastic bowl containing BOE solution and the bowl is covered. The solution is allowed to etch away the oxide for a time of 11 min. At this point, the oxide wafer is removed from the dish and rinsed in de-ionized water. The PR layer on top is now removed in an acetone bath. Then the wafer is rinsed successively with DI water, isopropyl alcohol and blown dried. The next step is the same as for silicon wafers where the Cu-Ni layer is sputtered. A feature of this approach is that the catalyst film is deposited on both the oxide as well as the silicon surface thereby permitting a

Fig. 4.4 Process flow for CVD growth on oxidized Si substrate.
A direct comparison between CVD growth under otherwise identical conditions on these two surfaces.

### 4.3 CVD Growth

The most important step is the growth of desired carbon layer. The Si or SiO$_2$ on Si samples with metal catalyst are now subjected to thermal chemical vapor deposition. The CVD system comprises of a Centigrade Systems Inc. furnace. The detailed experimental setup used for thermal CVD in this work is shown in Fig. 4.5. A 54” long quartz tube with an inner diameter of 3 inches is placed in the furnace where it is heated to high temperatures for carbon deposition. The Si or oxide on Si substrates of size 1 cm $\times$ 1 cm on which the 20 % copper-80 % nickel catalyst is sputtered are placed on quartz carrier boats inside the quartz tube. A bubbler with a heating coil wound around it is used for storing and heating cyclohexane as a source of carbon. The bubbler is usually heated to

![Fig. 4.5 Setup for thermal CVD.](image-url)
100 °C which is greater than the boiling point of cyclohexane at 81 °C. The gas feed line from the bubbler to the furnace tube is heated by a heating tape wound around the feed lines. Two mass flow controllers (MFCs) are used for setting the flow rates for the gases used. The argon tank is connected to both MFCs as argon is used first during annealing and then also for CVD growth cycles. In some cases, a 10 % hydrogen-90 % argon mixture has also been used in addition to argon for annealing and CVD. The tank with the Ar-H₂ mixture is connected to one of the MFCs. The flow rates in the two MFCs are usually set at 100 sccm each. A combination of a rotary pump and a turbo molecular pump is used for getting a good vacuum in the setup. Before starting the process, the bubbler is filled with 30 ml of cyclohexane and then the bubbler is carefully sealed. Care is first taken so that the two-way valves 1, 2 are open and the valves 3, 4 are closed in Fig. 4.5.

The carbon layer deposition procedure is started by pumping down the entire chamber to 300 mTorr with the vacuum pump. The pressure is monitored by a convectron gauge. After the roughing vacuum is obtained, the three-way valve 5, at the exhaust end is closed and the vacuum pump is switched off. The argon tank is now opened so argon starts filling up the tube. The vacuum pump is switched off. The pressure starts building up and reaches 1000 Torr, somewhat over the atmospheric pressure. Now, the exit valve 5, is opened to lower the atmospheric pressure to one atmosphere. The excess argon inside the chamber escapes and the pressure stabilizes at the atmospheric pressure or 760 Torr. The CVD growth is carried out at atmospheric pressure. The deposition temperatures are usually set between 550 and 800 °C and the CVD furnace heater is switched on at this point. The reactor usually takes 25-28 min to
reach 800 °C. Now, the catalyst films are first annealed at the growth temperature itself for 15-30 min. While the annealing is going on, the bubbler heating coil is switched on so the cyclohexane starts heating up and the bubbler reaches 100 °C. This usually takes 20 min. Once annealing is complete, valves 1, 2 are closed and valves 3, 4 in Fig. 4.5 are gently opened. Heated cyclohexane vapors are carried by the argon gas flow via heated tubing into the furnace for chemical vapor deposition. Carbon starts to deposit on the metal particles formed after annealing and the process is allowed to continue for 12-13 min after which the valves 3, 4 are closed so the flow of cyclohexane vapors is shut off. The bubbler heating coil is switched off and valves 1, 2 are opened again. The walls of the furnace also show deposition as the walls of reactor are at the same temperature as the substrate. This gives a wide deposition zone on the reactor walls and the substrate.

The furnace is kept on for 5-6 more min after switching off the flow of cyclohexane so that any vapors inside the chamber can complete deposition of carbon on the substrate or be pushed out by the argon flow. The quartz tube is allowed to cool down to room temperature by continuous argon flow. This usually takes 5-6 hours. The samples are removed at this point and the carbon films are ready for characterization.

The quartz tube is removed from the setup and cleaned with acetone spray. This removes the loose carbon strips attached to the furnace walls. After this, the walls inside are scrubbed with a long brush so the carbon sticking to the walls is removed. Finally, DI water is poured into the tube and the loose particles are emptied out along with the water. Even this process does not remove all the carbon stuck to the walls. The tube is re-inserted into the furnace and heated to a temperature of 850 °C for 50-60 min in air ambient so the remaining carbon on the walls is burned off.
5. RESULTS AND DISCUSSIONS

The chemical vapor deposition step is the most critical step in the process. Numerous CVD runs are hence conducted under different process conditions to determine the effect of the process parameters on the layer growth. As mentioned in the previous chapter, the growth temperature is varied between 550 \(^{0}\)C and 800 \(^{0}\)C. CVD runs and all annealing steps in this thesis are carried out at atmospheric pressure of 760 Torr. Argon gas is used as the carrier gas for most of the annealing and CVD runs while a 10% hydrogen / 90% argon mix is also used for some of the runs. Volume of the quartz tube used is approximately 2900 cc while the pumping speed of the rotary vacuum pump used is 50 cc/sec. The carbon growth on the samples is analyzed in a Hitachi S-3600N Variable Pressure SEM and EDAX EDS system. The hydrocarbon source used for CVD in this study is cyclohexane. Its vapor pressure is 97.6 Torr at 25 \(^{0}\)C. The bubbler with cyclohexane is heated to 100 \(^{0}\)C before opening the 2-way valves and letting argon carry the heated vapors into the chamber. Table 5.1 gives vapor pressure of cyclohexane up to a temperature of 200 \(^{0}\)C and these values are plotted in Fig. 5.1. At 100 \(^{0}\)C, cyclohexane

<table>
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<tr>
<th>Temperature ((^{0})C)</th>
<th>Pressure (Torr)</th>
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<tr>
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Table 5.1 Vapor pressures of cyclohexane at different temperatures. After reference [30]
vapor pressure is approximately 1310 Torr.

5.1 Effect of Growth Temperature Using Argon on Si Substrates

The optimum growth processing parameters for carbon rods, fibers and eventually, MWNTs needs to be determined. For this, initially the carbon layers are grown at 550 °C on Cu-Ni films 80-90 nm thick. The catalyst layers are sputtered by the E306A Edwards magnetron sputtering system using RF power at an operating pressure of 3-4 × 10⁻² Torr. The Cu-Ni films are deposited on silicon substrates and patterned by ultraviolet lithography as shown in Fig. 4.1 in the previous chapter. Annealing is carried out for 15 min at atmospheric pressure the growth temperature in argon with a flow rate
of 100 sccm prior to the CVD growth. Argon is also used as the carrier gas for
transporting heated cyclohexane vapors to the growth chamber. Effects of annealing time
and catalyst thickness will be discussed later in this chapter. Carbon films are deposited
on the patterned catalyst films formed on the silicon substrates. The carbon layer
obtained at 550 °C CVD growth temperature is shown in Fig. 5.2. It does not have any
noticeable structures and looks like an amorphous carbon (a-C) layer. This is probably
because of the low temperature. These layers peeled off when scratched with tweezers.

The CVD growth temperature is increased to 650 °C. All other process conditions
were kept the same except the catalyst anneal temperature which is now also increased to
650 °C. The carbon layer obtained is shown in Fig. 5.3. The layer shows growth without
revealing shapes under SEM, indicating that the growth to be still amorphous.

![SEM image of carbon layer deposited at 550 °C on Si substrate with Ar. Catalyst
thickness is 80-90 nm.](image)

Fig. 5.2 SEM image of carbon layer deposited at 550 °C on Si substrate with Ar. Catalyst
thickness is 80-90 nm.
The layer growth at higher temperature seems to be sparse but without much improvement otherwise. A further increase in the process temperature to 700 °C results in stunted growth as shown in Fig. 5.4. The growth is sparse and perhaps indicates that growth of carbon rods or rods from the metal particles may be just starting to form at this point. However, the optimum temperature for the growth of long fibers and rods has not been reached yet.

On increasing the growth temperature to 745 °C, a difference in the quality of the carbon structures is immediately seen. However, instead of carbon fibers, rods or nanotubes, a thick film of carbon globules stacked on top of each other is noticed. This is shown in Fig. 5.5. This kind of growth may be attributed to the thickness of the catalyst
Fig. 5.4 SEM image of carbon deposits at 700 °C on Si substrate with Ar. Catalyst film thickness is 80-90 nm.

Fig. 5.5 SEM image of carbon film deposited at 745 °C on Si substrate with Ar. Catalyst film thickness is 80-90 nm.
film which is still at 80-90 nm. The continuous film may not have split into small particles during the annealing prior to CVD growth. Thus, this may be a result of not having enough sites for CNT nucleation and, in turn leading to carbon atoms successively depositing on the relatively smooth film in the form of amorphous globules instead of diffusing through the metal particles. The latter process forms small diameter CNTs. Another factor may be that the chamber/substrate temperature is so high that self-pyrolysis of cyclohexane dominates the deposition. Due to this, amorphous carbon is deposited very quickly in the form of globules from the gas-phase precursor. This amorphous carbon then restricts the initiation of CNTs from the catalyst particles. Growth at a temperature of 790-800 °C is then performed to see if the same kind of growth seen at 745 °C would also be seen at this temperature. Thick growth with a higher density of globules than at 745 °C is also noticed for growth at 790 °C as shown in Fig. 5.6.

Fig. 5.6 SEM image of carbon globules seen at 795 °C on Si substrate with Ar. Catalyst film thickness is 80-90 nm.
Carbon globules deposited from the cyclohexane vapor phase are each around 1.2 µm in diameter. From the above runs conducted at different temperatures, the optimum temperature can be said to lie between 700 and 745 °C where the self pyrolysis of cyclohexane is least predominant.

Another process parameter which is important in addition to the process temperature is the catalyst layer thickness, whose effect is investigated in the following section.

5.2 Effect of Catalyst Thickness Using Argon

The thickness of Cu-Ni catalytic films used is varied from 2 nm to 80 nm for annealing between 710 °C and 750 °C, which from section 5.1 is considered the most optimum temperature range. The thinner catalytic films, less than 20 nm, are sputtered using an RF power of 200 W for less than 1 min on the patterned oxide-coated Si wafers with an oxide thickness of approximately 1.1 µm. More precisely, nominally 2 nm, 4 nm, 6 nm and 15 nm thick films are obtained by performing sputtering for 5 sec, 10 sec, 15 sec and 35 sec respectively. The effect of depositing the catalyst on the oxide and on the plain silicon surfaces is investigated by comparing the carbon growth on Cu-Ni catalyst on SiO₂ and on Si. The growth time for all the CVD runs is 12 min.

It is noticed that the carbon films with different carbon rods and tubes are deposited on the regions where there is the thin film of Cu-Ni present on silicon oxide. The growth on the regions on the substrate which had Cu-Ni catalytic film on bare silicon surface showed very short stunted nubs of carbon. This maybe due to Cu-Ni silicide formed on silicon inhibiting the formation of MWNTs and carbon rods.
The thicker Cu-Ni films are sputtered at 200 W on (100) oriented silicon wafers. In this case, carbon films are deposited on areas with Cu-Ni film on Si substrates. The diameter and length of the rods and fibers in each carbon film is determined from magnified SEM images by measuring dimensions for 10 cases where the structures have different sizes and finding the average readings. Annealing for all the catalyst films in this section is performed for 15 min in an argon flow of 100 sccm at the growth temperature.

When the Cu-Ni film thickness is 2 nm, the carbon films synthesized at 720 °C on oxide part of oxide-coated Si substrates consists of small scattered fibers/rods as shown in Fig. 5.7. This SEM image and the most of the following images look very similar to Fig. 3.6(b) where Lee et al. [20] had reported synthesis of carbon fibers using Cr. These short rods in Fig. 5.7 are approximately on average 60 nm in diameter and 690

![Fig. 5.7 SEM image of carbon rods grown at 720 °C with 2 nm thick Cu-Ni catalyst film on oxide-coated Si substrate with Ar.](image)
nm in length. This result shows that the catalyst film is thin enough to have split into metal islands whose average size is approximately 60 nm during annealing. Once the heated cyclohexane vapors are let into the chamber, the hydrocarbon atoms diffuse into the catalyst particles and on saturating the particle, start growing rods on top of the particles, seeming to exhibit a base growth mechanism where the particle stays at the bottom of the carbon rods.

When 4 nm thick Cu-Ni catalyst film is used, carbon rods are still noticed at 720 °C on the oxide surface after annealing in Ar for 15 min at the growth temperature. However, the rods now have average diameter of 70 nm and average length of 725 nm as shown in Fig. 5.8. This is in agreement with other papers in literature like Nureshev et al. [22] who have reported that when argon is used during their CVD process, the diameter and length of the carbon fibers observed are seen to increase with the thickness

![SEM image of carbon rods grown at 720 °C with 4 nm thick Cu-Ni catalyst film on oxide-coated Si substrate with Ar.](image)

Fig. 5.8 SEM image of carbon rods grown at 720 °C with 4 nm thick Cu-Ni catalyst film on oxide-coated Si substrate with Ar.
of the catalytic layer. In the case of 6 nm thick Cu-Ni catalyst film on patterned oxide-coated substrate, rods with average diameter of 130 nm and an average length of 960 nm are obtained on the oxide surface of the patterned oxide-coated substrate as shown in Fig. 5.9. The deposited rods are thicker and longer than the rods noticed for the previous cases. This result indicates that perhaps the catalyst film in this case, is splitting into islands which are approximately 100 nm in size and the thickness of the carbon rods increases with the thickness of the catalyst film used.

When a 15 nm catalyst films is used, the rods on the oxide surface have average diameter of 285 nm and average length of 2.5 µm as seen in Fig. 5.10. One difference between this case and the previous cases is that the density of the rods seen has

Fig. 5.9 SEM image of carbon rods grown at 720 °C with 6 nm thick Cu-Ni catalyst film on oxide-coated Si substrate with Ar.
Fig. 5.10 SEM image of carbon rods grown at 720 °C with 15 nm thick Cu-Ni catalyst film on oxide-coated Si substrate with Ar.

noticeably increased. Another observation is that the diameters and lengths of the rods have increased by a large extent. The results of growth on catalyst films upto 6 nm thick on oxide coated Si substrates in Figs. 5.7-5.9 indicate that using thin films produce metal particles and rods having diameters less than 150 nm at a temperature of 720 °C. Using 15 nm thick Cu-Ni film produces carbon rods having much larger diameters of 285 nm. For all cases, the carbon rods are seen to grow selectively on catalyst deposited on oxide surfaces rather than catalyst deposited on silicon substrates. For the growth of MWNTs to take place, it is essential that the metal islands formed for nucleation are as small as possible. The optimum catalyst film thickness in this case, necessary for growth of MWNTs is seen to be less than 15 nm.
These diameters and lengths of the carbon fibers for different Cu-Ni film thicknesses is plotted in Fig. 5.11 below. Both these dimensions are seen to increase with the catalyst film thickness. The length of the fibers grown is seen to increase rapidly with the Cu-Ni film thickness while the fiber diameter increases more gradually with Cu-Ni thickness.

![Graph showing the relationship between film thickness and length/diameter of carbon fibers.](image)

**Fig. 5.11** Average length and diameter of carbon fibers versus Cu-Ni film thickness on oxidized Si substrate.

For Cu-Ni films greater than 15 nm thick, the diameter and length will probably not increase because the Cu-Ni films will get too thick. The thick films, even after annealing in Ar might not separate into islands. Due to this, the carbon atoms might not be able to diffuse through the relatively smooth film and will not be able to produce fibers of length and diameter similar to the fibers produced for thinner Cu-Ni films [31].
The various types of growth seen in the above cases are for different catalyst thicknesses annealed in Ar for 15 min at 720 °C for CVD growth time of 12 min. From the results, the most suitable Cu-Ni film thickness should not exceed 15 nm for MWNT growth on oxidized wafers while using argon during annealing and as carrier gas. The metal particles formed when the annealing is performed, play an important role during the growth of rods or MWNTs during CVD. The sizes of the particles are determined here after annealing in argon and the argon/hydrogen mixture.

5.3 Effect of Annealing on Metal Particle Size for Different Catalyst Film Thicknesses

Thin catalyst films are sputtered on the patterned oxide coated wafers as shown in Fig. 4.4. The same catalyst film is deposited on both the silicon and the oxide surfaces at the same time. Annealing is then performed for samples in a 100 sccm argon flow for two durations of 15 min and 30 min at a temperature of 725 °C. The particle sizes on silicon surfaces are first determined from the SEM images.

5.3.1 Annealing Performed on Cu-Ni Film on Si in Argon

The nominal thicknesses of the catalyst films sputtered on silicon wafers are 6 nm, 12 nm and 24 nm. Using such thin films on silicon wafers is generally not preferred as the metal particles formed after annealing will not be stable on silicon surfaces. Also, the Cu-Ni alloy can react with the silicon and form silicides which might inhibit the growth of MWNTs during the CVD growth phase. Annealing of Cu-Ni films on silicon wafers is performed for both 15 min and 30 min duration at 725 °C to observe if any Cu-Ni particles are formed and if so, what their sizes are. It is observed that metal particles do form after the anneal step and that the average Cu-Ni particle size on Si wafers
increases as the Cu-Ni film thickness increases. This is similar to the results of Morjan \textit{et al.} [23] who used an argon-hydrogen mixture for growing MWNTs using iron catalyst deposited on oxidized wafers and reported that the catalyst particle size increases with increasing film thickness.

After the annealing is performed, SEM images of the nucleated particle surfaces are taken. For each image, the diameter of 20 particles is measured and the average size is obtained. Table 5.2 gives average particle size after 15 and 30 min anneal in Ar at 725 ⁰C for several Cu-Ni film thicknesses on Si substrate. Fig. 5.12 shows plots for the data given in Table 5.2. It is seen that the particle size for the same film thickness increases with anneal time. This is especially true for thin films, where the particles coalesce and combine to form larger particles with increasing annealing time. For the 15 min anneal case, the particle size for a 6 nm thick Cu-Ni film is 90 nm which increases to 139 nm for a 24 thick Cu-Ni film.

Table 5.2 Thickness of various Cu-Ni films on Si and their resulting average particle sizes after annealing at 725 ⁰C in Ar for 15 and 30 min.

<table>
<thead>
<tr>
<th>Thickness of film(nm)</th>
<th>Particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>12</td>
<td>156</td>
</tr>
<tr>
<td>24</td>
<td>139</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thickness of film(nm)</th>
<th>Particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>125</td>
</tr>
<tr>
<td>12</td>
<td>242</td>
</tr>
<tr>
<td>24</td>
<td>226</td>
</tr>
</tbody>
</table>
Similarly, for the 30 min anneal, the particles size increases from 125 nm for 6 nm thick Cu-Ni film to nearly 225 nm for a 24 nm thick Cu-Ni film. A phenomenon that is observed is that the particle size tends to slightly decrease for the 24 nm thin films compared to the 12 nm films for both the 15 and 30 min anneals. The reason the graphs flatten out for the 24 nm film maybe due to the fact that the catalyst film is so thick on the silicon surfaces that the particles cannot coalesce as much as the thinner films which causes the size of the particles to be almost equal to the particle size for a 12 nm film, even for the longer anneal time for 30 min.

![Graph showing average particle sizes versus pre-anneal film thickness for 15 min and 30 min anneals in Ar at 725 °C on Si substrate.](image)

Fig. 5.12 Average particle sizes versus pre-anneal film thickness for 15 min and 30 min anneals in Ar at 725 °C on Si substrate.
5.3.2 Annealing Performed on Cu-Ni Film on SiO$_2$ in Argon

Results similar to the Cu-Ni film on Si surfaces are also observed for Cu-Ni film on the oxide part of the SiO$_2$ coated Si substrate after the 15 and 30 min anneals at 725 °C. The average particle size increases with the Cu-Ni film thickness and also with the anneal time. The data is given in Table 5.3 and plotted in Fig. 5.13. The average particle diameter for a 15 min anneal increases from nearly 71 nm for a 6 nm thick Cu-Ni thin film to 186 nm for a 24 nm thick Cu-Ni film for the same anneal time. For a 30 min anneal, the particle size for the above catalyst thickness cases increases from 90 nm to 284 nm. Comparing results from annealing of Cu-Ni films on silicon and oxide coated Si wafers, for films equal to or less than 12 nm thick, the average particle size on oxidized wafers is smaller than for silicon wafers for the same anneal time. For 6 nm thick Cu-Ni thin films, the particle size is 90 nm for films on silicon wafers while it is reduced to 71 nm for films on oxidized wafers. In the case of the 12 nm thick Cu-Ni films, the catalyst

<table>
<thead>
<tr>
<th>CuNi on SiO$_2$-15 min anneal</th>
<th>Thickness of film(nm)</th>
<th>Particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>186</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CuNi on SiO$_2$-30 min anneal</th>
<th>Thickness of film(nm)</th>
<th>Particle size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>284</td>
</tr>
</tbody>
</table>
Fig. 5.13 Average particle size versus pre-anneal film thickness for 15 min and 30 min anneals in Ar flow at 725 °C on oxide-coated Si substrate.

Particle size is 156 nm on silicon surface and only 81 nm on the oxide surface. This is attributed to the Cu-Ni and oxide interactions which lead to the particles being smaller on silicon oxide compared to plain silicon. Cu-Ni silicide does not form during annealing in case of Cu-Ni films on oxide, which should aid the growth of MWNTs.

Another important observation is that the flattening out or saturation phenomena seen in the case of silicon wafers in Fig. 5.12 for higher values of Cu-Ni film thickness is not seen for the case of oxidized Si wafers. From Fig. 5.13, the coalescence phenomena continues for higher values of Cu-Ni film thicknesses deposited over oxide-coated substrate. The cases considered here are for catalyst films annealed in argon. The next
case considers Cu-Ni films annealed in a mixture of argon and 10% hydrogen and 90% argon flows.

5.3.3 Annealing Performed on Cu-Ni Films on SiO₂ in Argon and 90% Argon-10% Hydrogen

Annealing is performed using a mixture of argon at 100 sccm and 10% hydrogen-90% argon at 100 sccm for 15 min and 30 min at 725 °C. A mixture of 10% hydrogen-90% argon gas is introduced into the setup in Fig. 4.5 along with the argon flow used in the previous runs. The thin Cu-Ni films sputtered in this case are nominally 6 nm, 12 nm and 24 nm thick. These films are RF sputtered on patterned oxide wafers with the oxide thickness of 1.1 µm. From the previous results of annealing Cu-Ni films in argon on oxide coated wafers and Cu-Ni films on Si, we have seen that the average size of the Cu-Ni particles is smaller on oxide surfaces than on bare silicon. Hence, Cu-Ni particles formed on oxide surfaces after anneal in Ar-H₂ flow are the only ones investigated here.

Table 5.4 gives the average particle sizes from SEM analysis for different Cu-Ni film thicknesses as a function of 15 and 30 min anneal time in a mixture of H₂ and Ar at 725 °C. Fig. 5.14 gives a plot of the data given in Table 5.4.

Table 5.4 Thickness of various Cu-Ni films on SiO₂ coated samples and their resulting average particle sizes after annealing in Ar-H₂ flow at 725 °C.

<table>
<thead>
<tr>
<th>CuNi on SiO₂-15 min anneal</th>
<th>Thickness of film (nm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>214</td>
</tr>
<tr>
<td>CuNi on SiO₂-30 min anneal</td>
<td>Thickness of film (nm)</td>
<td>Particle size (nm)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>240</td>
</tr>
</tbody>
</table>
Fig. 5.14 Average particle size versus pre-anneal film thickness for 15 min and 30 min anneals at 725 °C on oxide surfaces in argon-hydrogen flow.

The average particle sizes for the case of the 6 nm catalyst film are compared to argon annealed cases in Table 5.3. For example, for the 15 min anneal case, the average size of the particles is 60 nm for 6 nm catalyst thin film for anneal in Ar-H₂ mixture. The corresponding values for anneal in argon yielded 90 nm for Cu-Ni on Si wafers and 70 nm for Cu-Ni on oxide part of SiO₂ coated Si wafers. Similarly for the 30 min anneal, the average particle size of 70 nm is slightly smaller for the anneal in Ar and H₂ mixture compared to the corresponding values of 125 nm and 90 nm for a 6 nm thick Cu-Ni film on Si and oxide coated sample respectively.
Similar results for a 6 nm thick film is also seen after the 30 min anneal. Here, the average particle size on oxide is 70 nm after annealing in Ar-H\textsubscript{2} mixture while it is 125 nm for Cu-Ni film on Si and 90 nm for Cu-Ni on oxide part of oxide-coated substrate for the Ar anneal cases. Fig. 5.14 also does not exhibit the saturation phenomenon that was seen in the case of Cu-Ni films on silicon in Fig. 5.12. This shows that when the 24 nm thick film on oxide is annealed in Ar-H\textsubscript{2}, coalescence continues to take place.

The average particle size in the case of 15 min anneal in Ar-H\textsubscript{2} mixture at 725 °C increases from 60 nm to 215 nm as the Cu-Ni film thickness is increased from 6 nm to 24 nm. For a 30 min anneal in Ar-H\textsubscript{2} mixture at 725 °C, the corresponding average particle size values increase from 70 nm to 240 nm. The results observed here are similar to the results in the previous two subsections of annealing in argon only where the particle size also increase with the film thickness and the anneal time. Though unlike the case for Si substrate, no saturation of average particle size with 24 nm thick Cu-Ni film is observed here.

Growth of MWNTs requires particle sizes equal to or less than 150 nm [20]. This suggests Cu-Ni film thickness needed in this research for growth of MWNTs and carbon rods seems to be equal to or less than 12 nm for both cases of anneal with argon and Ar-H\textsubscript{2} as seen from Tables 5.1-5.3. The Ar-H\textsubscript{2} anneal flow seems to produce the smallest alloy particles making this preferable to using only argon for the thinnest film case of 6 nm. Also, the annealing time necessary for producing MWNTs with diameters less than 150 nm while using 12 nm thin films seems to be 15 min or less.

CVD growth is carried out using heated cyclohexane vapors at 710-725 °C for a duration of 12 min with 15 min anneal in an Ar-H\textsubscript{2} mixture at the growth temperature.
with nominally 6 nm and 12 nm thick sputtered Cu-Ni films on patterned oxide wafers. They are annealed for 15 min in 100 sccm flow of Ar and 100 sccm flow of the Ar-H$_2$ mixture. The cyclohexane vapors are let into the tube by the argon flow at this point and carbon deposition is performed for 12 min. After the process is complete, the cyclohexane vapors are turned off along with argon-hydrogen mixture and the tube is allowed to cool down to room temperature in argon ambient prior to removing the samples.

5.4 Results of CVD growth in an Argon-Hydrogen Flow

The results of the CVD growth at a temperature in the range 710-725 °C in the case of 6 nm and 12 nm thick Cu-Ni films on oxide part of oxide-coated substrates are given in Figs. 5.15 and 5.16 respectively. As in the case of CVD growth discussed in section 5.2, the deposition on the bare silicon surface of the oxide-coated substrate

Fig. 5.15 SEM image of carbon rods/fibers grown at 725 °C in Ar-H$_2$ mixture on 6 nm thick Cu-Ni film on oxide-coated substrate.
showed only short, thick stubs of carbon. The reason for this as stated earlier is probably due to the formation of metal silicide which prevents growth of rods and MWNTs with the thin catalyst film used. From Fig. 5.15, the average diameters of the carbon rods and fibers observed seems to be in the range of 50-60 nm. This is approximately equal to the particle size of 60 nm obtained in Table 5.4. This may indicate that the carbon rods exhibit a base growth mechanism where the metal particle stays at the bottom of the carbon rod whose diameter is then nearly equal to the diameter of the particle formed after annealing. The length of the rods is about 1.1 µm. Comparing Fig. 5.15 to Fig. 5.9, it is seen that the latter which involved only argon flow showed structures with diameters of 130 nm compared to 60 nm structures for the former case with Ar-H₂ mixture processing. The deposition obtained after annealing in Ar-H₂ thus showed carbon
rods/fibers with smaller diameters and the conditions seem to be more suitable for the growth of MWNTs. When a 12 nm thick Cu-Ni film is used, as seen from Fig. 5.16, the carbon fibers are 160 nm in diameter with lengths of nearly 5 µm. This also nearly matches the average particle size value of 135 nm in Table 5.4. This also indicates that the base growth is responsible for deposition.

When compared with Fig. 5.10, the diameter of the carbon structures in Fig. 5.16 have reduced from 285 nm in case of the Ar flow to 130 nm for the Ar-H₂ flow, again making the latter case more optimum for the growth of MWNTs. The structures of the carbon fibers on the 6 nm and 12 nm thick Cu-Ni catalytic films are characterized by transmission electron microscopy (TEM). The close up TEM images of the side walls of the carbon fibers on 6 nm and 12 nm Cu-Ni films are shown in Figs. 5.17 and 5.18 respectively. Both images show that the structure of the carbon fiber in each case consisted of tubes. Graphitic planes along the edges of the walls are seen in both cases in the circled areas in Figs. 5.17 and 5.18. This indicates that MWNTs with walled structures have been produced. However, the crystalline nature of these MWNTs does not appear to be very good from these images.

An important observation about the internal diameter of the nanotubes can be made from the images. It is seen from Fig. 5.17 in case of the 6 nm thick Cu-Ni film, the diameter of the NTs is 50 nm. This is close to the average particle size of 60 nm observed in Table 5.4 for 6 nm thick Cu-Ni film seen after annealing in Ar-H₂ for 15 min. The value of 50 nm is also equal to diameter of the carbon fibers seen in the SEM image of Fig. 5.15. This shows that whatever the growth mechanism for this CNT is, its diameter is of the same magnitude as the average particle size of 60 nm in Table 5.4.
Fig. 5.17  TEM image of CNTs on 6 nm thick Cu-Ni film on oxide-coated substrate. Growth temperature of 725 °C in Ar-H₂ ambient.

Fig. 5.18  TEM image of CNTs on 12 nm thick Cu-Ni film on oxide-coated substrate. Growth temperature of 725 °C in Ar-H₂ ambient.
The behavior of the CNT having same magnitude as the Cu-Ni particle is also observed in case of the CNTs on the 12 nm thick Cu-Ni film. In this case, the diameter of the NTs is 130 nm, which is close to the average particle size of 135 nm given in Table 5.4 after 15 min Ar-H₂ anneal. Based on TEM and annealing results, the growth mechanism can be attributed to diffusion of carbon atoms diffuse into the metal catalyst particles resulting in NTs growing with the same diameter as the Cu-Ni particles [32].

5.5 Sheet Resistivity Measurements on Carbon Layers

Sheet resistivity measurements are performed on MWNTs grown on the 6 nm and 12 nm thick Cu-Ni films in the two cases discussed in subsection 5.4 in Ar-H₂ flow for the best growth conditions determined so far in this research. The resistance measurements involved 1) A 4-point probe method (Veeco FPP-100 station) and 2) ohmmeter.

For this measurement, 200 nm thick Al films are evaporated at the ends of samples in an NRC 703 thermal evaporator. These two thin metallic Al strips form contacts for measurements. The resistance is measured by an ohmmeter between the ends of the sample. The sheet resistivity \( R_S \) can then be determined from the resistance as \( R_S = R \times (W/L) \) where \( L \) =length, \( W \) =width. The length and width of the MWNTs/ Cu-Ni coated sample in each case are both equal to 1 cm. Therefore, this makes the sheet resistivity equal to the resistance value for each case.

The sheet resistivity readings are also taken directly from 4 point probe measurements on the two samples. The results for both these sets of sheet resistivity measurements are shown in Table 5.5.
Table 5.5  Sheet resistivity measurements for carbon deposits grown at 725 °C on 6 nm and 12 nm Cu-Ni films on oxide-coated substrates with Ar-H₂ flow mixture.

<table>
<thead>
<tr>
<th>Catalyst thickness (nm)</th>
<th>Sheet resistivity from ohmmeter measurement (ohm/square)</th>
<th>Sheet resistivity from 4 point probe measurement (ohm/square)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>243.5</td>
<td>293.3</td>
</tr>
<tr>
<td>12</td>
<td>56.3</td>
<td>65.6</td>
</tr>
</tbody>
</table>

The sheet resistivity of the carbon films decreases as the catalyst film thickness is increased. The decrease in the resistivity for carbon films corresponding to 12 nm thick Cu-Ni film is probably due to the fact that carbon fibers deposited are of better quality than for the 6 nm thick Cu-Ni film. Also, this maybe because longer carbon fibers are deposited in the case of the 12 nm thick Cu-Ni film which improves the conductance of the film [33].
6. SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 Summary and Conclusions

The purpose of this research is to investigate the behavior of cyclohexane as a carbon source in a CVD process. Different CVD growth temperatures are investigated for carbon layer deposition. CVD growth of carbon layers is carried out on both Si and SiO₂ coated Si substrates. A 20% Cu-80% Ni metal film is employed as a catalytic layer in this work. Suitable temperature for growth of CNTs utilizing 20% Cu-80% Ni catalyst films is determined. Effect of Cu-Ni film thickness for CNT growth is investigated. Average Cu-Ni particle size for different Cu-Ni film thicknesses after annealing in Ar and in Ar-H₂ is determined. CVD film growth is carried out with Cu-Ni film thicknesses which produce the smallest particles after annealing in Ar-H₂ at the growth temperature and the growth is characterized by TEM. Sheet resistance measurements are performed on the deposited carbon layers to examine the effects of morphology on resistance.

Initially, 80 nm thick Cu-Ni films as catalytic layers are sputtered on silicon wafers and annealed at growth temperatures for 15 min in argon at atmospheric pressure. CVD is performed using cyclohexane for 12 min for temperatures varying from 550 °C to 800 °C with argon as the carrier gas. At temperatures equal to or less than 650 °C, it is noticed that the carbon growth taking place tended to be amorphous. When the temperature approaches 700 °C, it is noticed that the amorphous growth tends to decrease dramatically and the growth of carbon in the form of rods or fibers starts. However, when the temperature is increased to 750 °C, the self pyrolysis effect is seen to dominate the process with carbon depositing in the form of globules with 1-2 µm diameter.
successively on top of each other. This suggests that temperature range of 700-750 °C may be the most suitable temperature range for growth of MWNTs and long carbon fibers and rods. The Cu-Ni silicide formed when the Cu-Ni reacts with the silicon surface maybe the reason for the absence of any noticeable CNT growth on Si substrates. This Cu-Ni silicide may inhibit growth of any CNTs.

In order to determine the effect of catalytic layer thickness and the nature of substrate on the grown layer quality, Cu-Ni catalytic layers ranging in thicknesses from nominally 2 nm to 80 nm are first sputtered on patterned oxide wafers. These wafers have regions of bare Si and oxide-coated Si surfaces exposed for carbon layer growth. As before, annealing is first carried out on all these samples in argon for 15 min at the growth temperature which in this case is 725 °C. CVD is then carried out using cyclohexane for 12 min at 725 °C. In all the subsequent cases discussed, short stubs of carbon is seen to deposit on the regions where there was Cu-Ni film on Si, probably due to the metal silicides formed inhibiting growth of CNTs and/or carbon fibers. For a 2 nm thick Cu-Ni film, carbon rods 60 nm in average diameter and 700 nm in average length are seen on the oxide surface. For 4 nm thick Cu-Ni catalytic layer, the average diameter and the average length of carbon rods on the oxide coated substrate increase to 70 nm and 725 nm respectively. In the case of 6 nm thick Cu-Ni film, the average diameter and average length of carbon rods on the oxide are 130 nm and 960 nm. These values increase sharply to 285 nm for average diameter and 2.5 µm for average length for a 15 nm thick Cu-Ni film on the SiO₂ surface.

From this study, the preferred thickness of the Cu-Ni film on oxide coated substrates resulting in smaller diameter particles is equal to or less than 15 nm. Using
thicker catalyst films reduces the possibility of producing catalyst particles small enough from which MWNTs can grow.

Three Cu-Ni films 6 nm, 12 nm and 24 nm in thickness are sputtered on the oxide and silicon surfaces on oxidized patterned Si wafers and annealed for 15 min and 30 min in argon flow and in argon-hydrogen flow at 725 °C. The latter is to examine effect of hydrogen as a reducing agent in the annealing process. In the case of 6 nm thick Cu-Ni film, the average size of catalytic particles is 90 nm on the silicon surface after the 15 min anneal in Ar at 725 °C. The average Cu-Ni particle size on bare silicon increases with the Cu-Ni film thickness to 156 nm for 12 nm thick Cu-Ni film after 15 min anneal in Ar at 725 °C. The particle size decreases slightly for the 24 nm thick Cu-Ni film on silicon surface after 15 min anneal in Ar at 725 °C to 139 nm. This is attributed to the Cu-Ni film thickness being too thick, due to which the degree of coalescence exhibited by the 24 nm thick Cu-Ni film decreases compared to the coalescence exhibited by the 6 and 12 nm thick Cu-Ni films after the anneal in Ar flow. The average Cu-Ni particle size for 6 nm thick Cu-Ni film on bare silicon is 125 nm after 30 min annealing in Ar flow. The trend for decrease in the average particle size for the 24 nm thick Cu-Ni film on silicon surface is also noticed for the 30 min anneal in Ar at 725 °C where the average particle size is 226 nm compared to 242 nm for the 12 nm thick Cu-Ni film case. Comparing these results, it is concluded that the particle size on Si substrate for each film increases with the annealing time and film thickness at annealing temperature of 725 °C.

The average particle size of the same Cu-Ni films described in the previous paragraph on oxide surfaces of the patterned oxide-coated substrate is also determined. For 6 nm thick Cu-Ni catalytic film, the average particle size is 71 nm on oxide surface
after 15 min anneal in Ar at 725 °C. This increases to 81 nm in the case of 12 nm thick Cu-Ni film on oxide. An increase in the average Cu-Ni particle size with film thickness at the temperature of 725 °C is also noticed in the case of 24 nm thick Cu-Ni film with the particle size being equal to 186 nm after 15 min anneal in Ar at 725 °C. This is in contrast to the results on Si substrate where average particle size decreased for the 24 nm thick Cu-Ni case. The phenomena of the average particle size increasing with annealing time is also observed here with the Cu-Ni particle size on oxide surfaces being 90 nm, 125 nm and 284 nm for the 6 nm, 12 nm and 24 nm thick Cu-Ni films after annealing in Ar for 30 min at 725 °C.

The average particle size on the oxide surfaces for each case of the 6 nm and 12 nm thick Cu-Ni films is smaller than the particle size of the same films on silicon after annealing in Ar at 725 °C. Therefore, after the 6 nm and 12 nm thick Cu-Ni films are deposited on patterned oxide coated substrates and annealed for 15 min and 30 min in Ar-H₂, the average particle size of each Cu-Ni film on oxide surface only is determined. The average Cu-Ni particle size, for Cu-Ni film below 12 nm thickness on silicon surface will be larger than the particle size on oxide surface and therefore may not be of help in growth of CNTs. The 6 nm and 12 nm thick Cu-Ni film produce average particle sizes of 60 nm and 135 nm respectively after 15 min anneal in Ar-H₂ at 725 °C. The Cu-Ni particle size increases further to 214 nm for the 24 nm thick Cu-Ni film. An increase in the average particle size with annealing time is observed in this case of annealing in Ar-H₂ at 725 °C with the particle sizes equal to 70 nm, 152 nm and 240 nm for 6 nm, 12 nm and 24 nm thick Cu-Ni films respectively for 30 min anneal time.
Comparing particle sizes for 6 nm, 12 nm and 24 nm thick Cu-Ni films after annealing in Ar and Ar-H\(_2\), the smallest average particle size of 60 nm is formed in the case of 6 nm thick Cu-Ni catalytic film on oxide surfaces when annealed in Ar-H\(_2\) at 725 0C for 15 min. The average particle size for 12 nm thick Cu-Ni film on oxide after 15 min anneal in Ar-H\(_2\) at 725 0C is 135 nm. This may also be suitable for growth of CNTs [16]. However, this particle size is larger than the corresponding value for 12 nm thick Cu-Ni film for Ar anneal. This indicates that the anneal time of 15 min or less for 6 nm thick Cu-Ni films in Ar-H\(_2\) flow is suitable though Ar anneal may also give comparable results.

CVD is carried out on the 6 nm and 12 nm thick Cu-Ni sputtered layers on oxide oxidized Si substrates at a temperature of 725 0C after annealing the samples for 15 min in argon-hydrogen ambient at the growth temperature. The 6 nm thick Cu-Ni sample yielded good carbon fibers 50 nm in diameter which resembled small diameter MWNTs. The 12 nm thick Cu-Ni sample produced approximately 160 nm diameter carbon fibers.

TEM analysis on the carbon fibers on the 6 nm and 12 nm show that the structures have diameters of 50 nm and 130 nm respectively. These dimensions match the average particle size of 60 nm and 135 nm for the 6 nm and 12 nm Cu-Ni thick films. This shows that the fibers have the same diameters as the particle sizes, indicating that growth of structures by the carbon atoms diffusing into the metal particles is taking place. The TEM images show the presence of tubular shapes with graphitic walls indicating that these structures are MWNTs, though of not very good crystalline nature.

Sheet resistivity measurements are performed by 4-point probe method and from ohmmeter measurements on the samples described above to estimate if there was any relation between the resistance and the carbon structures produced. These carbon layers
are deposited at 725 °C on 6 nm and 12 nm thick Cu-Ni catalytic films deposited on oxide-coated Si substrates and annealed in Ar-H₂ ambient at the growth temperature for 15 min. It is observed that the sheet resistivity reduces from 293 Ω/square for the sample with 6 nm Cu-Ni catalytic layer thickness to 85 Ω/square for the samples with 12 nm thick Cu-Ni catalytic layer from the 4 point probe measurements. The drop in the resistivity values maybe due to the deposited layer being more dense for the 12 nm thick Cu-Ni film compared to the 6 nm thick Cu-Ni catalytic film. The ohmmeter readings in both cases show somewhat smaller values than the 4 point probe readings.

Process parameters like the growth temperature, Cu-Ni catalyst thickness, annealing gas ambient and annealing time have thus been narrowed down by the research conducted in this thesis to achieve CNT growth.

6.2. Future Work

Although 50-60 nm carbon fibers and carbon rods have been synthesized in this work, there are some parameters which need to be investigated further to produce better quality MWNTs and carbon fibers. First, a furnace with a better temperature control is desired. Second, the catalyst used is an alloy comprising of 20% copper-80% nickel. This composition is chosen as vertical filament-type nanotubes have been produced with this composition. Other catalytic film materials need to be investigated in conjunction with cyclohexane carbon source. Third, the effect of the CVD growth pressure on the nature of carbon growth needs investigation. Only atmospheric pressure CVD is examined in this work. Fourth, the use of pure hydrogen or hydrogen rich ambient during annealing and growth should be researched to see if smaller metal particles and vertically aligned MWNTs can be produced. Introduction of hydrogen though 10% hydrogen-90% argon
anneal gas decreases the diameter of grown carbon tubes indicating that further study on
grown layers with different hydrogen concentration is required.
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