Investigation of catalyst composition for cobalt and iron catalysts on the chirality of grown single walled carbon nanotubes

Master`s Thesis within the Master`s program in Physics

By: Saeed Motaragheb Jafarpour

SUPERVISOR
Dr. Hamidreza Barzegar Goltapehei

EXAMINER
Dr. Thomas Wågberg

Department of Physics
Umeå University
Umeå, Sweden
Abstract

The synthesis of type-enriched semiconducting or metallic single-walled carbon nanotubes (sc/m-SWCNTs) with high quality by means of catalytic chemical vapor deposition (CCVD) are essential prerequisites for implementing of SWCNTs into nanodevices. In particular, the Fe–Co bimetallic catalysts system is promising due to its ability to grow SWCNTs by CCVD. However, there is still a gap in understanding how to adjust catalyst composition aiming further improvements in SWCNTs properties with respect to the electronic type. In particular, formation of well-defined nanoalloy of bimetallic catalysts during catalyst conditioning as well as its impact on SWCNTs growth are not clearly understood. Here we present a systematic investigation on effects of catalyst composition based on different Molar ratios of Fe:Co catalysts on the properties of CCVD grown SWCNTs using Raman spectroscopy. After CVD growth of SWCNTs on different molar ratios of Fe:Co, We find that by using molar ratio of Fe:Co=1:1.5, growth of SWNTs that are strongly dominated by two types of semiconducting tubes, the (7,5) and (12,1) tubes, can be achieved.
# Table of Contents

Chapter 1 ........................................................................................................................................................................... 5

**Introduction to carbon nanotubes** ........................................................................................................................................ 5

1.1 Introduction ................................................................................................................................................................. 5

1.2 CNTs Theory ................................................................................................................................................................. 6


1.2.1 Types of CNTs ......................................................................................................................................................... 6

1.2.2 Structure of SWCNT ............................................................................................................................................... 7

1.2.3 Synthesis of CNTs .................................................................................................................................................... 8

1.2.4 CVD method ............................................................................................................................................................ 10

1.2.5 Catalyst preparation ................................................................................................................................................ 13

1.3 Measurement techniques ........................................................................................................................................... 14


1.3.1 Raman spectroscopy ............................................................................................................................................. 14

1.3.2 X-ray photoelectron spectroscopy ......................................................................................................................... 19

Chapter 2 ........................................................................................................................................................................... 21

**Experimental** ............................................................................................................................................................... 21


2.1 Catalyst preparation .................................................................................................................................................... 21

2.2 Preparation of Si Substrate .......................................................................................................................................... 23

2.3 Catalyst deposition by dip-coating process .................................................................................................................. 25

2.4 Calcination ................................................................................................................................................................... 26

2.5 CVD setup .................................................................................................................................................................... 26

Chapter 3 ........................................................................................................................................................................... 29

**Results and Discussions** ................................................................................................................................................ 29

3.1 XPS result .................................................................................................................................................................... 29


3.1.1 Identification of catalysts molar ratio ..................................................................................................................... 29

3.1.2 Effect of Calcination ............................................................................................................................................... 31

3.2 Raman spectroscopy results ....................................................................................................................................... 33


3.2.1 Qualitative Raman .................................................................................................................................................. 33
Chapter 1

Introduction to carbon nanotubes

1.1 Introduction

Carbon is known to be the most versatile element that exists on the earth. It has different properties which can be used in variety of applications depending on how the carbon atoms are arranged [1,2]. Carbon in the form of graphite was discovered in 1779, and 10 years later in the form of diamond [3]. 200 years later, Smalley et al. discovered fullerenes, recipients of 1996 Nobel Prize in Chemistry for the discovery of fullerenes [4]. The discovery of fullerene, the fact that carbon could form stable and ordered structure apart from graphite and graphene, motivated researcher all around the world to do more research on carbon structures[5].

In 1991, Sumio Iijima, discovered a new cylindrical carbon structure known as carbon nanotube (CNTs) that contained at least two layers (double-walled carbon nanotubes, DWCNTs), or many more layers (multi-walled carbon nanotubes, MWCNT) [6]. Two years later, in 1993, a new type of CNTs with just a single layer known as single-walled carbon nanotube (SWCNTs) was observed by him [7].

From the structural point of view, CNT is a one dimensional tubular form of carbon nanostructures with hexagonal arrangement of carbon atoms. The diameter of CNTs varies in nanometer range and length can be up to several micrometers (the length to diameter ratio is about 1000) [1]. These cylindrical carbon nanostructures have exceptional properties that make them potentially useful in nanoscale electrical and mechanical devices. Due to high carbon-carbon bond strength, CNTs have known as one of the strongest materials in the nature. In addition, they can exhibit different electrical properties depending on their structure. Due to these exceptional properties and the possibility to integrate them in various devices, CNTs became an interesting subject for scientists and industries. In addition, there is a great interest on improving the quality of produced CNTs with predefined structures or properties for different applications [3].

In this work, we used dip-coating techniques to efficiently deposit nano-sized metal catalysts on Si substrate. Since the diameter of the CNTs is mainly determined by the
size of the catalyst nanoparticles, the prepared Si substrates with nano-sized catalysts can be used to grow SWCNTs. Effect of different molar ratios of Fe and Co in the catalyst solution are investigated systemically in order to study the influence of catalyst compositions on the chirality restrictions of gown SWCNTs in CVD. In order to determine the chirality of grown SWCNTs, Raman analysis based on several different excitation wavelengths is applied. Our results give insight into the mechanisms of selective (chirality or electronic type) growth of SWNTs that can be future utilized SWNTs in applications, especially when a high selectivity of SWNT types is important such as sensors and transistors [8].

## 1.2 CNTs Theory

### 1.2.1 Types of CNTs

A Single-walled carbon nanotubes (SWCNTs) can be imagined as a graphene rolled into a cylindrical shape (Figure.1.1a), with a diameter of about 0.7-2 nm [7]. On the other hand, a collection of concentric SWCNTs with different diameters is known as multi-walled carbon nanotubes (MWCNTs) as shown in Figure.1.1b. The length and diameter of these MWCNTs as well as their properties are very different from those of SWCNTs [6]. Due to single layered structure and bonding conditions, SWCNTs exhibit unique properties which are not distinguished by MWCNTs. They can be either semiconducting or metallic depending on their geometrical structures and diameter. Therefore, synthesize of high-quality SWCNTs with specific diameter and structure is essential for further application in nanodevices [9]. Moreover, the special case of MWCNTs, double-walled carbon nanotubes (DWCNTs) must be emphasized here because depending on structure they may exhibit similar morphology and properties as compared to SWCNTs [10].

![Fig.1.1: (a) SWCNTs and (b) MWCNTs](image-url)
1.2.2 Structure of SWCNT

A SWCNT can be imagined as a graphene sheet which is rolled to form a tube. For detail analysis, first a vector $C_h$ is defined in the graphene sheet. This vector can be described in terms of unit vectors of the graphene sheet $a_1$ and $a_2$ as shown in Fig.1.2.

$$C_h = na_1 + ma_2$$

Where $n$ and $m$ are two integers. Now if the graphene sheet is rolled in such a way that the end and tip of the vector $C_h$ coincide, then the resulting SWCNT can be specified by set of integers $(n,m)$. The vector $C_h$ is called chiral vector and the angle $\theta$ between $C_h$ and $a_1$ direction is called chiral angle and it varies between 0 to 30 degree. The set of integers $(n,m)$ for each specific SWCNT is called the chirality of the SWCNT. A nanotube which is constructed in this way called a SWCNT with chirality of $(n, m)$. Fig1.2 shows how a hexagonal graphene is rolled to form SWCNTs in a vector structure classification [9].

Depending on the manner in which the graphene is rolled up (the chirality $(n, m)$), the arrangement of carbon atoms along the cylinder circumference can be “arm-chair” with $m=n$ ($\theta=0$), “zig-zag” with $m=0$ ($\theta=30$) or several different intermediate “chiral” with $(n,m)$ ($0<\theta<30$) structures(Fig1.2) [9].

Fig.1.2: Structure of SWCNTs
The length of the chiral vector \((C_h)\) is the circumference of the CNT and is given by the corresponding relationship:

\[
c = |C_h| = a\sqrt{(n^2 + nm + m^2)}
\]

Where the value “\(a\)” is the length of the unit cell vectors \(a_1\) or \(a_2\). “\(a\)” is related to the carbon–carbon bond length \(a_c\), in carbon nanotube structure, \((a_c = 0.144 \text{ nm} \ [13])\) by the relation:

\[
a = |a_1| = |a_2| = a_c \sqrt{3}
\]

Using the circumferential length \(c\), the diameter of the CNT is thus given by the relation:

\[
d = c / \pi
\]

In addition, Chiral angle \(\theta\) (The angle between the chiral vector and \(a_1\)) can be defined by:

\[
\theta = \tan^{-1}(m\sqrt{3})/(m + 2n)
\]

As a result, the structure of SWCNTs can completely determine by the pair of integers \((n, m)\) which is related to the chiral vector. On the other word, it is possible to use these integers to drive most of the SWCNTs properties. For example SWCNTs with \(|n-m| = 3i\) are metallic, and those with \(|n-m| = 3i \pm 1\) are semiconducting, (where \(i\) is an integer) [9].

1.2.3 Synthesis of CNTs

Carbon nanotubes are generally produced by three main techniques: arc discharge [11], laser ablation [12], and chemical vapor deposition (CVD) [13].

Arc discharge technique uses two graphite electrodes placed close to each other (separated by approximately 1mm). An electric potential is then applied in order to produce an arc discharge between these two electrodes in a chamber that is usually filled with inert gas at low pressure. The discharge vaporizes the surface of one of the electrodes, and forms a rod-shaped that deposit on the other electrode. Production of CNT in this method depends on the uniformity of arc plasma and the applied temperature [11].
In the laser ablation technique, a pulsed laser vaporizes a graphite target at high temperature reactor while an inert gas (such as argon) is bled into the chamber. Then the resulting vaporized carbon condenses on the cooler surfaces of the reactor in form of nanotubes as well as other nanoparticles [12].

In Chemical vapor deposition, a carbon precursor decomposed over catalyst materials (usually a transition metal or a mixture of them) at high temperature (depending on type of the carbon precursor and catalyst materials) resulting in the growth of CNTs over catalyst materials [13,14].

Table 1.1 shows a summary of the three common techniques for the synthesis of carbon nanotubes.

<table>
<thead>
<tr>
<th>Arc Discharge Method</th>
<th>Chemical Vapor Deposition</th>
<th>Laser Ablation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical yield 30 to 90 %</td>
<td>Typical yield 20 to 100 %</td>
<td>Typical yield up to 70%</td>
</tr>
<tr>
<td>The method can easily produce both SWNTs and MWNTs</td>
<td>Easiest method to produce large scale SWNTs</td>
<td>This method can produce SWNTs with good diameter control</td>
</tr>
<tr>
<td>This method is less expensive</td>
<td>This method is less expensive</td>
<td>This method is very expensive</td>
</tr>
<tr>
<td>The reaction product is not very pure and it requires further purification</td>
<td>The reaction product is quite pure</td>
<td>The reaction product is quite pure</td>
</tr>
</tbody>
</table>

Almost all different synthesis methods result in the growth of SWNTs with different diameters, quality and chiralities. It is desirable, for many applications, to produce a special type of nanotubes, such as metallic or semiconducting. In addition, for some applications, nanotube with well-defined individual chirality (see previous section for an explanation of SWNTs chirality) are needed [49]. On the other hand, Various Methods that used in production of SWNTs lead to products with contaminations such as residual catalyst and other forms of carbon and secondary processes are necessary to provide final products (SWCNTs) of sufficient purity [15–17].
1.2.4 CVD method

Nowadays, the CVD method is considered as the only economically suitable process and easy to scale up for CNT production and the integration into various devices. CVD offers better control on the growth parameters for synthesizing CNTs at low temperature and ambient pressure directly on the substrate or wafer. On the other hand, this method generally produces a complex mixture of carbon nanostructure materials, including SWCNTs, MWCNTs and amorphous carbon. Therefore, purification of final product is an unavoidable process step [18,19].

A typical CVD set up is schematically shown in Fig.1.3. The process involves passing a suitable carbon precursor (such as hydrocarbon) vapor through a tubular reactor in which a catalyst material is present at sufficiently high temperature (600–1200 C) to decompose the hydrocarbon. CNTs grow on the catalyst in the reactor, which are collected after cooling the system to room temperature [15].

In order to have better overview of CNTs growth during the CVD process, it is important to understand their growth mechanism that is still an open question. There are several researches that scientists considered different growth mechanism for CNTs regarding to the growth methods that they used, but it is approved that in general, the growth mechanics for CNTs using CVD method can be divided in three main steps [20–23]:

1. Decomposition of carbon precursor (such as hydrocarbon) vapor over the surface of catalyst particles.

2. Dissolution of carbon atom in the catalyst particles and making a supersaturated solution.

3. Diffusion of carbon through the catalyst particles and Precipitation (formation) of carbon atoms in tubular form.

4. Termination of CNT growth after a certain time (Figure.1.4)
According to different experiments, Scientists reported that catalyst nanoparticles can be observed at the tip or root (base) of the CNTs that can introduce two different models for CNTs growth mechanism. Catalyst nanoparticles observed at root of CNTs leading to base growth models while catalyst nanoparticles are seen at the tip of CNTs leading to a tip growth model (Figur.1.5) [24].
CNTs synthesis by CVD are strongly affected by the experimental parameters such as type of the hydrocarbon, type, size and composition of catalyst, substrate, growth temperature, growth pressure, gas-flow rate and growth time. However, to keep our discussion compact, here we will consider only the three key parameters: hydrocarbon, catalyst and substrate [24].

1.2.4.1 CNT Catalysts

CNT synthesis by CVD techniques requires the introduction of suitable metal catalysts in the form of nanoparticles. Most commonly-used metal catalysts are Fe, Co, Ni because of two main reasons: (i) high solubility of carbon in these metals at high temperatures; and (ii) high carbon diffusion rate in these metals. Besides that, high melting point and low equilibrium-vapor pressure of these metals offer a wide temperature window of CVD for a wide range of carbon precursors [25].

In addition, there are several studies showing that the diameter of the grown CNTs is related to the size of the used catalyst particles [26]. In general, when the catalyst particle size is few nanometers, SWCNT forms (Having small catalyst particle is essential for SWCNT growth but clearly is not enough); whereas larger catalyst particles favor MWCNT formation. Therefore, finding a suitable method to deposit catalyst particle with the ability of controlling the size of the catalyst particles is one of the main issue to control the type and diameter of the grown CNTs (discuss later) [24,27].
1.2.4.2 Substrate

Substrates permit controlling the metal nanoparticle sizes. In addition, it improves the growth of aligned CNTs as a function of the particle dispersion. The catalysts can be deposited on the substrates from solution, electron beam evaporation or by physical sputtering [28]. Commonly used substrates in CVD are, quartz [29], silicon [30,31], silicon carbide [16,32].

1.2.4.3 Carbon source (Precursors)

A variety of gaseous and liquid hydrocarbon is used to produce CNTs via CVD. The type of hydrocarbon sources varies from light gases such as C₂H₄ and C₂H₂ to heavier liquids like benzene [15,18,21,24]. The carbon sources in the form of liquids are vaporized before introducing into the reaction chamber. To avoid the oxidation of the carbon, the chamber is kept free of oxygen during the production process.

1.2.5 Catalyst preparation

In order to have a uniform growth of CNTs, the substrate has to be homogenously coated with catalyst particles with uniform size. The catalyst materials can be directly deposited on the substrate in the form of particles, or a smooth thin film of catalyst material [28].

In addition, Guo et al. [19] observed the fact that the diameter of the carbon nanotubes depend on the thickness of the deposited metal film on the substrate. Therefore, among several methods of coating such as electron beam evaporation, spin coating, sputtering, lithography and dip-coating, dip-coating method is known as a simple method to coat a large variety of substrates by a wide range of coating materials. This method is capable of controlling the thickness of the coated layer down to the nanoscale [33].

1.2.5.1 Dip-coating

Dip-coating is a simple and well-known technique that has been used for several decades in industry and laboratories. This method can be used to coat different substrates with a thin layer of different materials. In summary, when a plate (substrate) is vertically withdrawn from a liquid bath, parts of the solution remain on the surfaces of the plate as a liquid film. Depending on the experimental conditions (withdrawal speed and concentration of the solution), the evaporation of the solvent results in the formation of a
uniform distribution of solid particles or a smooth film of the solute on the substrate (Fig.1.6) [33,34].

![Fig.1.6: Schematic of dip-coating process](image)

### 1.3 Measurement techniques

As discussed before, the properties of carbon nanotubes vary with the individual SWNT chirality. Since SWNTs are produced as mixture of different chiralities, the properties of the synthesized material will depend on the proportions of different chiralities present in the sample. Many measurement techniques have been applied to determine the structure of SWNT materials. These range from observational techniques such as SEM, TEM and AFM to spectroscopic techniques such as UV-Vis- NIR, Photoluminescence, and Raman spectroscopy [35].

#### 1.3.1 Raman spectroscopy

Raman spectroscopy is one of the powerful analytical techniques for characterizing SWNTs. Raman spectra are used to determine tube diameter, chirality and electronic properties in both bulk and isolated nanotube samples [36]. Fig.1.7 shows a Raman spectrometer.
1.3.1.1 Working principle

Raman spectroscopy is based on Raman scattering discovered in 1928 by Raman et al. It is based on inelastic scattering between an incoming light and the studied material. During the scattering event, first an electron is exited from its valance energy band to the conduction energy band by absorbing a photon then an exited electron can be scattered by emitting phonon and finally the electron relaxes back to its valance band by emitting a photon. We generally observe the Raman spectra for the scattered photon. By measuring the intensity of the scattered light as a function of frequency down shift of the scattered light, the Raman spectroscopy plot can be drawn. Raman scattering can happen for photon emission by photon absorption, and these two processes are known stokes process and anti-stokes respectively [9,36,37].
1.3.1.2 CNT characterization by Raman Spectroscopy

There are three important bands (peaks) in Raman spectra of SWCNT. Fig.1.5 shows a Raman spectrum of a SWCNT in which we can see well defined G-bands which is related to two-dimensional graphite. G-bands consist of two main peaks. One related to the vibration of carbon atom along the axis of the nanotube which is known as $G^+$, the other is due to the vibration of carbon atoms along the circumference of a SWCNT referred to $G^-$. $G^+$ peak can be found around 1590 cm$^{-1}$ while $G^-$ is around 1570 cm$^{-1}$. There is also a band around 1350 cm$^{-1}$ that is known as the D-band. The D-band comes from a hybridized vibrational mode associated with graphene edges and it indicates the presence of some disorder to the graphene structure. This band is often referred as the disorder or defect band. There is another series of bands appearing at the low frequency (100-300 cm$^{-1}$) of the spectrum known as Radial Breathing Mode or RBM bands. The RBM correspond to the expansion and contraction of the tubes. The frequency of these bands can be correlated to the diameter and chirality of SWCNT [36–38].

Among these three areas of the Raman spectrum, the Radial Breath Mode (RBM) that related to the vibration of the carbon atom in radial direction (it seems that the nanotube breathing) observed approximately with frequency ($v_{RBM}$) between 100 to 300 cm$^{-1}$ is
unique for SWNTs and can be used to determine tube diameter [RBM is the one who shows to be more sensitive to the SWCNTs diameter] (d_t) through its frequency (ν_{RBM}). In addition, it can be used to check if there is any SWCNT in as-grown CVD sample through the presence of RBM picks in the Raman spectra [39].

![Raman spectrum of SWCNTs using 633 nm wavelength](image)

**Fig1.5:** Typical Raman spectrum of SWCNTs using 633 nm wavelength

In order to find the diameter of SWCNTs by using the ν_{RBM}, the following relation can be applied:

\[
ν_{RBM} = \frac{A}{d_t} + B
\]

Where, \(d_t\) is the SWNT diameter in nm and \(ν_{RBM}\) is the wave number in cm\(^{-1}\). A and B are experimentally determined parameters. The values of A and B are not always the same and change from isolated SWCNT to bundles of SWCNTs. This formula is exact when 1 nm <\(d_t\) < 2 nm.

Usually, most of the tubes self-assemble into bundles and radial modes are very sensitive to the nanotube packing. In order to calculate the SWCNTs diameter by considering the van der Waals interactions between the tubes (bundles), A=234 cm\(^{-1}\) nm and B=10 cm\(^{-1}\) nm.

In addition, in case of isolated SWCNTs, The nanotube diameters can be obtained by the RBM frequency as follow:
\[ d_i = \frac{A}{\nu_{RBM}} \]

Where \( A = 248 \) for the isolated SWCNTs [40].

It is worth to mention that by comparing two relations for isolated SWCNTs and bundles of SWCNTs, it can be understood that the parameter \( B \) that appears in the first equation (bundles of SWCNTs), insert the effect of bundling to the \( \nu_{RBM} \).

It is important to note that to get a complete picture of all chiralities that present on as-grown CVD sample; several lasers with different excitation energies must be used. It is obvious that a single Raman measurement at one wavelength just gives an idea about the SWCNTs that are in resonance with that laser. By using many laser lines (wavelengths), it is possible to have a complete diameter and chirality distributions of grown SWCNTs on the sample.

### 1.3.1.3 Kataura Plot

Kataura Plot, as shown in Figure 1.6, plotting the band gap energies as a function of the diameter of the SWNTs (and hence the wavenumber) [41]. It helps to determine the diameter and chirality \((n, m)\) of each SWCNTs by using the laser energy that is applied in Raman measurement (in eV) and the \( \nu_{RBM} \) (wave number in cm\(^{-1}\)) that observe in the Raman spectra [37,40].
1.3.2 X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS), is widely used as characterization technique for surface analysis of chemical composition in a sample. Generally, in XPS technique a sample is irradiated with mono-energetic x-rays at ultra-high vacuum condition, causing photoelectrons to be emitted from the surface of sample (Fig.1.7). The X-rays ionized the surface atoms and electrons from the core orbital are emitted with specific kinetic energies. The binding energy of the emitted electrons (known as photoelectrons) can be measured as the difference between the X-ray energy and kinetic energy of the photoelectrons. The XPS counts the number of photoelectrons with specific energy by using an electron energy analyzer. From the binding energy and intensity of a photoelectron peaks, the elemental identity, chemical state, and quantity of an element are determined. In addition, due to the low penetration ability of the photoelectrons through matter, the information given by XPS is usually limited to the atoms on the surface of the sample [42–44].
Fig. 1.7: Basic components of XPS system
Chapter 2
Experimental

2.1 Catalyst preparation

The aim of this study was to examine the effect of catalyst nanoparticles composition on chirality of the grown SWCNTs using CVD method. As the catalyst nanoparticles with suitable size is crucial important for CVD synthesis of SWCNTs, the first step in experimental work is catalyst nanoparticle preparation. In order to prepare catalyst nanoparticles, dip-coating method is utilized to deposit the catalyst materials, mixture of iron and cobalt, on silicon substrate.

In a typical experiment, iron (III) nitrates Fe(NO3)3 and cobalt (II) nitrate Co(NO3)2 (Fig.2.1) (both 99.999% purity from Alfa Aesar) were used as catalyst materials (precursors). In addition, ethanol (99.5% purity) was used as a suitable solvent in other to prepare our solution.

![Fig.2.1: Iron (III) nitrate Fe(NO3)3 (left) and cobalt (II) nitrate Co(NO3)2 (right)](image)

In order to study the effect of catalyst nanoparticles compositions on the grown SWCNTs, a systematic study on different molar ratios of iron and cobalt (II) nitrate in ethanol were investigated separately. As an example, in order to have a solution with equal molar ratio of Fe and Co (Fe:Co=1:1) two 10x10^{-3} molar (10 mM) solutions of iron (III) nitrate and cobalt (II) nitrate in 10ml ethanol were prepared. Then two prepared solutions were mixed together to make a solution with 10 mM concentration in 20 ml ethanol (Fig.2.2)
Concentration of the final solution should be always fixed around 10mM (according to the experimental condition) and can be calculated by the following relation:

\[ C_{\text{final}} = \frac{C_1 V_1 + C_2 V_2}{V_1 + V_2} \]

Where \( C_1 \) and \( C_2 \) are the concentration of iron and cobalt in each solutions before mixing them together respectively. \( V_1 \) and \( V_2 \) are the volumes of each solutions that were fixed at 10 ml always. The only variable in the above equation is the molar concentration of each catalysts that is define as a corresponding weight \( X \) (gr). The procedures that explained above for making the mixture are summarized in table 2.1.

![Image](image.png)

**Fig.2.2**: 10x10^{-3} molar (10 mM) solutions of iron (III) nitrate or cobalt (II) nitrate in 10ml ethanol

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol volume</td>
<td>10 ml</td>
<td>10 ml</td>
</tr>
<tr>
<td>Metal concentration</td>
<td>( C_1 ) mM</td>
<td>( C_2 ) mM</td>
</tr>
<tr>
<td>Metal amount</td>
<td>( X_1 ) gr</td>
<td>( X_2 ) gr</td>
</tr>
</tbody>
</table>

After mixing two solutions together, In order to have a uniform and homogenous mixture of catalysts, the mixture was sonicated for 30 min in the ultrasonic bath. As the temperature of the solution increase due to the sonication, the solution was left in the ambient temperature for 10 minutes to become stable and rich the ambient temperature.

22
Then, the prepared mixture was transferred to a beaker with 30 mm diameter and 60 mm height. The height of the solution in the beaker was 35 mm.

In order to study the effect of catalyst compositions on the grown SWCNTs, Different solutions of iron and cobalt with different Molar concentrations of each catalyst (solute) was prepared. As shown in Table.2.1, depend on the molar concentration (C₁ for Iron and C₂ for Cobalt) of each catalysts, appropriate amount(X) of each catalyst is measured by the balance and used in the each solutions. The concentration of the final solution (after mixing the two solutions of Iron and Cobalt in Ethanol together) must be 10 Mm according to the previous experimental conditions that leads to grow SWCNTs. Table.2.2 shows the different ratio of Iron and Cobalt that used in this project.

<table>
<thead>
<tr>
<th>Concentration of Fe in the solution</th>
<th>Concentration of Co in the solution</th>
<th>Fe:Co molar ratio in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM</td>
<td>10 mM</td>
<td>1:1</td>
</tr>
<tr>
<td>11.25 mM</td>
<td>9 mM</td>
<td>1.25:1</td>
</tr>
<tr>
<td>12 mM</td>
<td>8 mM</td>
<td>1.5:1</td>
</tr>
<tr>
<td>14 mM</td>
<td>7 mM</td>
<td>2:1</td>
</tr>
<tr>
<td>15 mM</td>
<td>5 mM</td>
<td>3:1</td>
</tr>
<tr>
<td>2*10 mM</td>
<td>-----</td>
<td>Fe</td>
</tr>
<tr>
<td>9 mM</td>
<td>11.25 mM</td>
<td>1:1.25</td>
</tr>
<tr>
<td>8 mM</td>
<td>12 mM</td>
<td>1:1.5</td>
</tr>
<tr>
<td>7 mM</td>
<td>14 mM</td>
<td>1:2</td>
</tr>
<tr>
<td>5 mM</td>
<td>15 mM</td>
<td>1:3</td>
</tr>
</tbody>
</table>

2.2 Preparation of Si Substrate

P-type silicon wafers with a thickness of 0.5 mm is used in this project as a support layer for catalyst. In order to prepare the silicon substrate for series of experiments, silicon wafer was cut to the dimension of approximately 8x35 mm to get several substrates with the similar size. Figure.2.3 shows the silicon substrate after cutting in proper dimension.
One of the most important issues two grow SWCNTs is to make silicon surface as clean as possible. The reason is contaminations and small particles that remain in the silicon substrate after cutting can lead to produce amorphous carbon and will decrease the purity of the grown SWCNTs. Therefore, the desired silicon substrate after cutting was cleaned in acetone by means of ultrasonic cleaner for 5 min followed by ultraviolet ozone cleaning for another 5 min to have much cleaner substrate. In addition ultraviolet ozone cleaning will make the surface of silicon substrate more hydrophilic and increase the wettability of the silicon substrate during the dip-coating process. Figure 2.4 shows the UV and ultrasonic cleaner that used for cleaning the substrate.
2.3 Catalyst deposition by dip-coating process

In order to make a thin film of the catalyst on the substrate, the cleaned Silicon substrate that was cut to the suitable dimensions (8 mm × 35 mm × 0.5 mm) was attached to the clip of the dip-coating set-up and the beaker that containing the prepared solution was placed under the substrate. The input voltage of the setup was fixed on 11 V with respect to the desired withdrawal velocity 4 cm/min [33]. Then, the setup was switched on. When 25 mm of the height of the substrate submerged in the solution, the setup was switched off. The substrate was left in the solution for 4 min and then it was withdrawn with the desired velocity (4 cm/min). The thin film of catalysts was deposited on the substrate while it was pulled up from solution. Finally, the solvent was evaporated and a thin layer of catalyst particles was formed on the substrate. Fig. 2.4 shows Dip-coating setup that used in this project. In addition, Table 2.3 shows the parameters that were used for Dip-coating procedure.

![Dip-Coating setup](image)

**Table 2.3: Dip-coating Parameters**

<table>
<thead>
<tr>
<th>Dip-coating Parameters</th>
<th>values</th>
</tr>
</thead>
<tbody>
<tr>
<td>current</td>
<td>1 mA</td>
</tr>
<tr>
<td>voltage</td>
<td>11 V</td>
</tr>
<tr>
<td>Velocity</td>
<td>4 cm/min</td>
</tr>
<tr>
<td>Time of process</td>
<td>5 min</td>
</tr>
</tbody>
</table>
2.4 Calcination

Calcination (thermal treatment process in presence of air) was used to the middle part of coated Si substrate with thin film of catalysts to burn the contaminations and undesirable component like carbon and nitrogen. In addition, After Calcination, the metal catalyst particles were changed to metal oxide. It is worth to notice that calcination process normally applied at temperatures below the melting point of catalyst particles. Fig.2.5 shows the oven that has been used for the calcinations process and the working parameters are listed in table.2.4.

![Oven for calcination](image)

**Fig.2.5:** Oven for calcination

<table>
<thead>
<tr>
<th>Calcination parameters</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>400°C</td>
</tr>
<tr>
<td>Heating time</td>
<td>15 min</td>
</tr>
<tr>
<td>Cooling time</td>
<td>15 min</td>
</tr>
</tbody>
</table>

2.5 CVD setup

The CVD setup used in this work consists of a quartz tube of the length of 110 cm and the outer diameter of 2.8 cm which passes through a furnace (ETF 30/12 H-V from Entech) as shown in figure 7. The furnace can be heated up to 1200°C.
There are four gas lines that can be used during the CVD process. Argon and Varigon can be used as carrier gases, Ammonia can be used in the setup as a support gas (not used in this project) and acetylene is used as carbon source. The flow rate of the gases can be controlled by four flow meters manually (Figure.2.6). Figure.2.7 shows The CVD setup was used to grow SWCNTs on catalysts coated Si substrate.

**Fig.2.6:** Gas lines and Flow meter

**Fig.2.7:** CVD setup for growing SWCNTs
In a typical CVD process, the Catalyst coated Si substrate was transferred inside the quartz tube in such a way that it was placed at the center of the furnace. Then the substrate was heated in Ar with 140 ml/min flow rate until it was reached 800 °C. After substrate reached 800 °C, Pretreatment step was started by adding 60 ml/min Ar/H2 to the Ar flow for 7 min. The growth of SWCNTs was carried out by adding 20 ml/min acetylene gas to the gas flow for 20 min. Before removing the sample, the system was cooled with pressured air to below 150°C. Experimental parameters for the growth of SWNTs are described in tables.2.5

<table>
<thead>
<tr>
<th>Process step</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Flow rate (mL/min)</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>RT-800</td>
<td>30</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>Annealing</td>
<td>800</td>
<td>7</td>
<td>140</td>
<td>60</td>
</tr>
<tr>
<td>Growth</td>
<td>800</td>
<td>20</td>
<td>140</td>
<td>60</td>
</tr>
<tr>
<td>Cooling</td>
<td>800-150</td>
<td>110</td>
<td>200</td>
<td>0</td>
</tr>
</tbody>
</table>

These procedures for catalyst preparation and CVD growth were used for different molar ratios of catalysts. Prior to the catalyst preparations and after growth of SWCNTs, different characterization methods such as Raman and XPS were utilized.
Chapter 3
Results and Discussions

3.1 XPS result

3.1.1 Identification of catalysts molar ratio

XPS analysis was used in order to confirm the presence of iron and cobalt on the coated substrates (qualitative XPS). The substrates which were coated by different molar ratio of catalyst particles were analyzed by XPS in the chemistry department.

One of the main issues in this project was to confirm the existence of ratio of Iron with the desired molar concentration after depositing on Si substrate by dip-coating process. To confirm this idea, three samples that coated with dip-coating by certain molar ratio of iron and cobalt in the solution were selected and then these samples were sent to the XPS for the measurements. The molar ratio of Iron and cobalt in these three selected samples are shown in table.3.1.

| The concentration of Iron and Cobalt in the final prepared solution |
|-------------------------|-------------------|------------------|
| Fe:Co                   | Fe:Co             | Fe:Co            |
| 3:1                     | 2:1               | 1.5:1            |

Figure 1 shows two XPS spectrum of three coated samples with different molar ratio Fe:Co. The signals between 711-733 eV and between 781-793 eV are related to Fe 2p and Co 2p respectively that confirm the existence of deposited metal catalysts on the substrate. In additions, the spectra showed significant amounts of carbon and oxygen on the sample. It is believed that these are related to some organic components which remained on the substrate after coating and some contamination from the environment as the XPS measurement was done ex-situ.
After XPS measurement was performed on the Samples, by using quantitative XPS, the amount of Iron and cobalt on the samples can be determined using peak analyzing as it is shown in figure 3.2.
According to the quantitative XPS results, it is acceptable if we assume that Fe:Co molar ratio in the prepared solution is the roughly same as their Molar ratio on the coated Si substrates by dip-coating method using the same solution as it is shown in Table.3.2.

Table 3.2: Result of XPS Measurements for 3 different substrates with different Fe:Co ratios

<table>
<thead>
<tr>
<th>Line</th>
<th>Fe:Co 3:1</th>
<th></th>
<th>Fe:Co 2:1</th>
<th></th>
<th>Fe:Co 1.5:1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Co 3p 3/2</td>
<td>781.3</td>
<td>2.35</td>
<td>25.36</td>
<td>781.0</td>
<td>2.45</td>
<td>37.27</td>
</tr>
<tr>
<td>Fe 2p 3/2</td>
<td>711.5</td>
<td>2.4</td>
<td>74.64</td>
<td>711.4</td>
<td>2.7</td>
<td>62.73</td>
</tr>
<tr>
<td>Fe:Co</td>
<td>2.94 : 1</td>
<td>1.67 : 1</td>
<td>1.59 : 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.2 Effect of Calcination

In order to find the effect of calcination on the Molar ratio of Fe:Co, a piece of the silicon substrate was coated with Molar ratio Fe:Co = 2:1 by Dip-coating technique. Then it divided in 2 pieces. One piece of the substrate heated in air at 400°C (calcination) for 15 minutes while the other piece didn’t meet the calcination. XPS measurement was done on these two substrates to study the effect of calcinations on the Molar ratio of Fe:Co.

The XPS analysis showed that the amount of carbon was decreased after calcination process. In addition, the results of quantitative XPS showed that calcinations of the catalyst coated Si substrate didn’t have significant effect on the molar ratio of Fe:Co on the substrate and the ratio remains approximately the same before and after calcinations (table.3.3, figure.3.3).
**Fig. 3.3:** XPS spectra for Fe:Co = 2:1, before and after calcination

**Table 3.3:** Result of XPS Measurements for calcination effect

<table>
<thead>
<tr>
<th>Line</th>
<th>Fe:Co 2:1 Before Calcination</th>
<th>Fe:Co 2:1 After Calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE, eV</td>
<td>FWHM, eV</td>
</tr>
<tr>
<td>Co 3p 3/2</td>
<td>781.2</td>
<td>2.35</td>
</tr>
<tr>
<td>Fe 2p 3/2</td>
<td>711.6</td>
<td>2.55</td>
</tr>
<tr>
<td>Fe:Co</td>
<td>1.67:1</td>
<td></td>
</tr>
</tbody>
</table>


3.2 Raman spectroscopy results

3.2.1 Qualitative Raman

As grown SWCNTs on the Si substrate were directly used in the Raman spectrometer. Before starting the measurement, the set-up was calibrated using the sharp peak of pure silicon at 520 cm\(^{-1}\). By using the camera of the instrument, the laser beam was focused on the desired part on the substrate. The accumulation and time of the measurements as well as the range of the spectra were defined through the software. Additionally, a software tool for cosmic ray removal was applied. The measurements were done using two different lasers with wavelengths of 785 nm and 633 nm. Mapping measurements was applied over 30 points due to scan larger area of the substrate and all the measurements has been done in the center of each substrate. The result of mapping measurements for each substrate was transferred to the Origin software in order to get the average spectrum and background subtraction. Then the background subtracted average spectrum was plotted for both 633nm and 785nm in each case.

The growth of SWCNTs was confirmed by the presence of a sharp and strong G peak and radial breading modes (RBM) in the recorded Raman spectra. Figures.3.4&5 show the Raman spectra of produced SWCNTs for Fe:Co=1:1.5 using two different Raman excitation wavelengths the 633 nm and 785 nm lasers. Each Raman excitation wavelength showed different RBM peaks at different frequencies. Figures.3.6 shows the mapping spectra over 30 points and the corresponding ravage spectrum in RBM region for two different lasers with wavelengths of 785 nm and 633 nm.
Fig. 3.4: Raman spectrum of SWCNTs using a laser with wavelength 633 nm

Fig. 3.5: Raman spectrum of SWCNTs using a laser with wavelength 785 nm
The RBM peaks are in the frequency range of 100 - 300 cm$^{-1}$. By using equation $\omega_{RBM} = A/d_t + B$ (where A and B are 223.5 cm$^{-1}$ nm and 10 cm$^{-1}$), it can be determined that the diameter of the tubes ($d_t$) are in the range of 0.79 - 1.7 nm.

The above procedures have been done for different as-SWCNTs substrate with different molar ratio of iron and cobalt by using two different Raman excitation wavelengths the 633 nm and 785 nm lasers.

### 3.2.1 Quantitative Raman

In order to find the position, intensity and integrated area for peaks in RBM region of Raman spectrum, a reliable peak fitting procedure is required. Peaks in a spectrum may sometimes need to be described by different functions. For instance, some peak is best described by a Lorentzian function while the other is best described by a Gaussian function. Using the Peak Analyzer tool, one can easily assign a different function to each peak, and then perform fitting on all peaks simultaneously. A more complex combination of Gaussian and Lorentzian lines is the Voigt profile. In this project, PeakFit software was used as a peak analyzer tool and Voigt profile was applied as the best function for fitting the SWCNTs peaks in RBM region. Figure 3.6 shows an example of peaks analyzing for an average spectrum in RBM region of Raman spectra. As it is shown in the Figure, 14 peaks can be determined by Voigt profile as a fitting function. Using this procedure, all information regarding each peaks (center, intensity, integrated are under each peaks) can be determined for all peaks in RBM region.
As it was discussed in chapter 2, the goal of this project is to investigate the effect of different molar ratio of cobalt to iron catalysts on the chirality of resulting grown SWCNTs. Due to achieve this goal, we only focus on the RBM region (100 - 300 cm\(^{-1}\)) of the Raman spectra in order to correlate the different catalyst compositions of Fe and Co to the abundance of different grown SWCNT chiralities. Figure 3.8&9 show the RBM region for the different molar ratios of Fe:Co after CVD (chapter 2) using 633 nm and 785 nm laser excitations. Different peaks in each spectrum related to different SWCNTs with different diameter and chiralities. Some of the peaks are more important because they show significant changes as the molar ratios change. Therefore, only these peaks were considered for details analyzing. It is worth to mention here that the peak in 303 cm\(^{-1}\) position is related to Si peak and it was not considered as a SWCNT peak.

Using the experimental Kataura plot and considering the resonance width of ± 0.1 eV for each wavelength, distinct ranges for semiconducting and metallic RBMs are determined as is shown in Figure 3.7. In addition, using the center position of the each peak in the Raman spectrum (peak analyzing) at RBM region, one can assign each peak to a suitable chirality by help of Kataura plot for each excitation energy (Table 3.4&5).
Qualitative observations of Figure 3.8 & 9 revealed that for different investigated molar ratios of Fe to Co, SWCNTs growth were confirmed by presence of peaks in RBMs region. In addition, the most highlight Molar ration was devoted to Fe:Co = 1:1.5 as in this composition, not only growth of semiconducting SWCNTs is observed by 633nm wavelength, but also growth of only semiconducting SWCNTs is confirmed by 785nm wavelength. As a result, selective growth of semiconducting SWCNTs is achieved by using catalysts with Molar ration of Fe:Co = 1:1.5.
Fig. 3.9: RBM spectra of grown SWCNTs for the prepared molar ratios (chapter 2) using 785 nm laser excitation.

Table 3.4: Chirality for selected SWCNTs using 633 nm laser excitation

<table>
<thead>
<tr>
<th>RBM(cm⁻¹)</th>
<th>282</th>
<th>262</th>
<th>251</th>
<th>195</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic type</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Chirality</td>
<td>(7,5)</td>
<td>(7,6)</td>
<td>(10,3)</td>
<td>(13,4)</td>
<td>(12,6)</td>
</tr>
</tbody>
</table>

Table 3.5: Chirality for selected SWCNTs using 785 nm laser excitation

<table>
<thead>
<tr>
<th>RBM(cm⁻¹)</th>
<th>268</th>
<th>235</th>
<th>225</th>
<th>215</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic type</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Chirality</td>
<td>(10,2)</td>
<td>(12,1)</td>
<td>(10,5)</td>
<td>(9,7)</td>
</tr>
</tbody>
</table>
In order to determine the abundance of each chirality that is grown on Si substrate after CVD, quantitative analyzing of Raman spectra in RBM region was used. As it is mentioned before, although there are several RBM peaks in each wavelengths, only the intense RBM peaks that are listed in Table.3.4&5 were considered. Using PeakFit software, integrated area over the all peaks in RBMs region can be determined for each wavelength. Table.3.6 is shown the center point, integrated area and type of fitting profile for all peaks in RBM region of only Fe catalyst at 633nm wavelength. By subtracting the integrated are over Si (red line) peak from total integrated are, integrated area over only SWCNTs can be determined [45,46].

\[
\text{Int. Area over all SWCNTs} = \text{Total Int. Area} - \text{Int. Area over Si}
\]

Finally, an estimation for abundance of each chirality \((n,m)\) can be determined by:

\[
\text{Abundance of } (n,m) = \frac{\text{Int. Area over } (n,m)}{\text{Int. Area over all SWCNTs}}
\]

Using above procedure, an estimation for abundance each chirality in terms of integrated area under the peak of selected chiralities can be determined and listed in Table.3.7&8. In addition, Figure.3.8 is shown the integrated area over selected chiralities as well as Si peaks for both wavelengths.
Table 3.6: Center point, integrated area and fitting profile of RBM for only Fe catalyst at 633 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Centroid</th>
<th>Int. Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Voigt</td>
<td>153.33</td>
<td>248.76</td>
</tr>
<tr>
<td>2</td>
<td>Voigt</td>
<td>167.48</td>
<td>428.71</td>
</tr>
<tr>
<td>3</td>
<td>Voigt</td>
<td>177.21</td>
<td>669.05</td>
</tr>
<tr>
<td>4</td>
<td>Voigt</td>
<td>184.36</td>
<td>3488.04</td>
</tr>
<tr>
<td>5</td>
<td>Voigt</td>
<td>190.39</td>
<td>17475.97</td>
</tr>
<tr>
<td>6</td>
<td>Voigt</td>
<td>195.92</td>
<td>19884.13</td>
</tr>
<tr>
<td>7</td>
<td>Voigt</td>
<td>222.29</td>
<td>7509.86</td>
</tr>
<tr>
<td>8</td>
<td>Voigt</td>
<td>246.35</td>
<td>514.07</td>
</tr>
<tr>
<td>9</td>
<td>Voigt</td>
<td>251.58</td>
<td>2712.76</td>
</tr>
<tr>
<td>10</td>
<td>Voigt</td>
<td>261.60</td>
<td>19932.90</td>
</tr>
<tr>
<td>11</td>
<td>Voigt</td>
<td>282.57</td>
<td>24676.66</td>
</tr>
<tr>
<td>12</td>
<td>Voigt</td>
<td>292.93</td>
<td>3743.55</td>
</tr>
<tr>
<td>13</td>
<td>Voigt</td>
<td>302.17</td>
<td>30809.56</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>135310</strong></td>
</tr>
</tbody>
</table>
Table 3.7: Chirality and integrated area for selected SWCNTs using 633 nm laser excitation

<table>
<thead>
<tr>
<th>RBM(cm⁻¹)</th>
<th>Chirality</th>
<th>282 (7,5)</th>
<th>262 (7,6)</th>
<th>251 (10,3)</th>
<th>195 (13,4)</th>
<th>190 (12,6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Fe:Co)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>M</td>
<td>S</td>
</tr>
<tr>
<td>Fe</td>
<td>(1:3)</td>
<td>0.24</td>
<td>0.20</td>
<td>0.02</td>
<td>0.20</td>
<td>0.17</td>
</tr>
<tr>
<td>(1:2)</td>
<td>0.29</td>
<td>0.14</td>
<td>0.06</td>
<td>0.05</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>(1:1.5)</td>
<td>0.07</td>
<td>0.06</td>
<td>0.03</td>
<td>0.40</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>(1:1.25)</td>
<td>0.47</td>
<td>0.15</td>
<td>0.04</td>
<td>0.01</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>(1:1)</td>
<td>0.34</td>
<td>0.12</td>
<td>0.05</td>
<td>0.12</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>(1.25:1)</td>
<td>0.25</td>
<td>0.10</td>
<td>0.05</td>
<td>0.16</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>(1.5:1)</td>
<td>0.36</td>
<td>0.12</td>
<td>0.05</td>
<td>0.07</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.8: Chirality and integrated area for selected SWCNTs using 785 nm laser excitation

<table>
<thead>
<tr>
<th>RBM(cm⁻¹)</th>
<th>Chirality</th>
<th>268 (10,2)</th>
<th>235 (12,1)</th>
<th>225 (10,5)</th>
<th>215 (9,7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Fe:Co)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Fe</td>
<td>(1:3)</td>
<td>0.16</td>
<td>0.43</td>
<td>0.20</td>
<td>0.06</td>
</tr>
<tr>
<td>(1:2)</td>
<td>0.03</td>
<td>0.54</td>
<td>0.27</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>(1:1.5)</td>
<td>0.12</td>
<td>0.36</td>
<td>0.16</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>(1:1.25)</td>
<td>0.13</td>
<td>0.67</td>
<td>0.11</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(1:1)</td>
<td>0.01</td>
<td>0.56</td>
<td>0.28</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>(1.25:1)</td>
<td>0.03</td>
<td>0.67</td>
<td>0.18</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(1.5:1)</td>
<td>0.04</td>
<td>0.54</td>
<td>0.22</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.10: Integrated area over selected chiralities for 785nm (left) and 633nm (right) wavelengths
3.2.3 Comparisons

Figure 3.11 and Table 3.9 shows the abundance of each chirality (n,m) for 8 different molar ratios of Fe:Co catalysts in terms of integrated area under the peak. As we can see, the amount of produced SWCNTs with different chirality were changed by using different Molar ratio of Fe to Co catalyst. For the SWCNTs that appear in 282 cm$^{-1}$ and 195 cm$^{-1}$ for 633 nm wavelength, a significant changes in respect to the different molar ratios of catalysts was observed. In addition, changing of catalyst composition of Fe:Co did not have much influence on the abundance of SWCNT that appear at 251 cm$^{-1}$ for 633 nm and 215 cm$^{-1}$ for 785 nm wavelength.

On the other hand, one can look at the maximum and minimum amount of produced SWCNTs in each molar ratios as shown in Table 3.9. As it shown in the tables, the maximum amount of produced SWCNTs is shown by and the minimum amount of produced SWCNTs is shown by colors. For example in case of (7, 5) SWCNT, the minimum amount of this tube was produced in Fe:Co=1:2 molar ratio while the maximum amount of this tube was produced in Fe:Co=1:1.5 molar ratio. In addition, It can be seen from the table that the Molar ration of Fe:Co=1:2 is an optimum ratio for selective growth of (13,4) nanotubes that is considered as a metallic SWCNTs. Moreover, in case of Fe:Co=1:1.5 molar ratio, the abundance of metallic SWCNTs are really low and the majority of grown SWCNTs are semiconducting with (7,5) and (12,1) chirality. Therefore, this molar ratio is more favorable for growth of predominantly semiconducting SWCNTs.
Table 3.9: Integrated area under different chiralities at 633nm and 785nm laser excitations

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>633 nm</th>
<th>785 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBM (cm(^{-1}))</td>
<td>282 (7,5)</td>
<td>262 (7,6)</td>
</tr>
<tr>
<td>Chirality</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>(Fe:Co)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>(1:3)</td>
<td>0.29</td>
<td>0.14</td>
</tr>
<tr>
<td>(1:2)</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>(1:1.5)</td>
<td>0.47</td>
<td>0.15</td>
</tr>
<tr>
<td>(1:1.25)</td>
<td>0.34</td>
<td>0.12</td>
</tr>
<tr>
<td>(1:1)</td>
<td>0.25</td>
<td>0.10</td>
</tr>
<tr>
<td>(1.25:1)</td>
<td>0.24</td>
<td>0.10</td>
</tr>
<tr>
<td>(1.5:1)</td>
<td>0.36</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Figure 3.11: Abundance of different chiralities at 633 nm and 785 nm laser excitations
3.3 Reproducibility

To confirm the reproducibility of the obtained results, two selected molar ratios (1:1 and 1.5:1) is considered for reproducibility test. Therefore, during the CVD process development, three CVD process with three substrates that were coated with similar molar ratio were performed. The results of CVD processes in each molar ratio are plotted in Figure.3.12 for Fe:Co=1:1 and Figure.3.12 for Fe:Co=1.5:1. The results revealed that our method for catalysts preparation as well as CVD processes have an acceptable degree of reproducibility as no dramatic changes in the integrated area under the peak was observed.

Fig.3.12: Result of Reproducibility in 1:1 ratio for 3 processes during the project. 633 nm (left), 785 nm (right)

Fig.3.13: Result of Reproducibility in 1.5:1 ratio for 3 processes during the project. 633 nm (left), 785 nm (right)
3.4 Conclusions

Recent works regarding selective growth of SWCNTs (electronic types or chirality) are shown the crucial effect of catalysts composition and catalyst treatments as well as catalyst preparation method on selective growth of SWCNTs using CCVD [47–50]. In the direction of these recent works, Here, we showed that by using dep-coating techniques for transferring catalysts from solution to the Si substrate, the molar ratio of Fe:Co in the solution maintained and XPS results confirmed the similar molar ration in the coated substrate compared to prepared solution. In addition, the molar ratio of Fe:Co was remained unchanged after calcination steps compared to coated Si Substrate. As a results, it is possible to have roughly defined molar ratio of Fe:Co on the Si substrate before CVD process.

From qualitative observation of Raman spectra, it was revealed that by using different molar ratio of Fe to Co, growth of SWCTs was observed by presence of peaks in RBM region. In addition, changing the molar ratio of Fe to Co had dramatic influence on the intensities (or integrated area) of peaks in RBM region (SWCNTs chiralities). In other word, by changing the molar ratio of Fe to Co, some chiralities are more favorable to grow with higher amount.

Finally, toward the electronic type selective growth of SWCNTs, It was shown that by using Fe:Co=1:1.5 Molar ratio, the abundance of metallic SWCNTs are really low and the majority of grown SWCNTs are semiconducting with (7,5) and (12,1) chiralities.

In conclusion, we have shown that by tuning the catalyst composition (Molar ratio of Fe:Co) as well as precise control over dip-coating process, in a certain Molar ratio (Fe:Co=1:1.5) we can have the growth of SWNTs that are strongly dominated by two types of semiconducting tubes, the (7,5) and (12,1) tubes. These results give better understanding to the mechanisms of selective growth of SWNTs (electronic type of chirality selective growth) and more highlighted the influence of catalysts composition.
References


