ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION OF TRANSPARENT AND CONDUCTIVE THIN FILMS OF SINGLE WALLED CARBON NANOTUBES

M.Sc. THESIS

İpek ÇAKMAK

Department of Nanoscience & Nanoengineering

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Thesis Advisor: Prof. Dr. Nilgün KARATEPE YAVUZ

May 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRANSPARAN VE İLETKEN TEK DUVARLI KARBON NANOTÜP İNCE FİLMLERİN HAZIRLANMASI

YÜKSEK LİSANS TEZİ

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Mayıs 2015

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Date of Submission : 4 May 2015
Date of Defense : 27 May 2015

FOREWORD

I would like to express my sincere gratitude to my supervisor Prof. Dr. Nilgün Karatepe Yavuz for her time, advices and encouragement through this study.

My special thanks to my family, for their full support and love me with all my decisions.

May 2015

İpek Çakmak

Physicist

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ABBREVIATIONS

CNT	**:** Carbon Nanotube
SWCNT	**:** Single Wall Carbon Nanotube
MWCNT	**:** Multi Wall Carbon Nanotube
CVD	**:** Chemical Vapour Deposition
PECVD	**:** Plasma Enhanced Chemical Vapor Deposition
CCVD	**:** Catalytic Chemical Vapour Deposition
AFM	**:** Atomic Force Microscope
SEM	**:** Scanning Electron Micposcope
TEM	**:** Transmission Electron Microscopy
TGA	**:** Thermogravimetric Analysis
nm	**:** Nanometer
UV	**:** Ultraviolet
OLED	**:** Organic Light Emitting Diodes
LCD	**:** Liquid Crystal Displays
ITO	**:** Indium Tin Oxide
AgNW	**:** Silver Nanowire
C_h	**:** Chiral Vector
T	**:** Primitive Translation Vector
DMF	**:** Dimethyl Formamide
NMP	**:** Dimethyl Pyrrolidone
SDS	**:** Sodium Dodecyl Sulfate
SDBS	**:** Sodium Dodecyl Benzene Sulfonate
HNO_3	**:** Nitric Acid
NaOH	**:** Sodium Hydroxide
C_2H_2	**:** Acetylene
MCE	**:** Mixed Cellulose Ester
$SOCl_2$	**:** Thionyl Chloride

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PREPARATION OF TRANSPARENT AND CONDUCTIVE THIN FILMS OF SINGLE WALLED CARBON NANOTUBES

SUMMARY

Carbon nanotubes (CNTs) are today one of the key elements of nanotechnology and are most intensively investigated materials. CNTs are a unique material with their high mechanical, electrical, optical, thermal and chemical properties that may be useful in a number of applications. The versatile properties of carbon nanotubes make its suitable for use in various transparent and conductive optoelectronic devices. Transparent and conductive electrodes are being utilized in solar cells, organic light emitting diodes (OLEDs), touch panels and many other optoelectronic devices. Among them indium tin oxide (ITO) is one of the most common materials. However, flexible, cost effective, conductive and robust single walled carbon nanotube (SWCNT) thin films can be preferred as an alternative to ITO electrodes. In addition, SWCNT thin film coating process does not need a vacuum system that can be applied at low temperatures via all solution based methods on several substrates over large areas. Spray and spin coating methods are more suitable deposition techniques for larger area applications. SWCNT thin films can easily be scaled up by utilizing a practical spray and spin coating setup for making transparent electrodes or thick SWCNT layers for other applications.

In this thesis, transparent and conductive electrode was fabricated using SWCNTs. SWCNTs were firstly synthesized by chemical vapor deposition of acetylene on Fe/MgO catalyst at 800°C and purified by 3M HNO_3 at 98.39 % purity level. Vacuum filtration and spray coating methods were utilized for the deposition of SWCNT. Several dispersing agents were investigated in order to achieve a homogeneous SWCNT solution, which were used in vacuum filtration and spray coating. After thin film deposition, optoelectronic properties were examined for different densities of SWCNT, surfactant and sonication procedure. Tip and bath sonicators were utilized due to homogeneous dispersion of SWCNT solution. In addition, acid and heat treatments were applied due to enhance the electrical conductivity of thin films. When compared to acid treatment and heat treatment, it has been found that heat treatment was more effective method to enhance optoelectronic properties of SWCNT thin films. The fabricated SWCNT thin films were characterized by scanning electron microscopy (SEM) and UV-vis spectrophotometer. Two point probe were utilized to determine the sheet resistance of SWCNT thin films on glass substrates that were deposited via vacuum filtration and spray coating methods. Thus, the efficiencies of thin films with fabricated different production parameters were determined and compared.

In recent years, silver nanowires (AgNWs) have been receiving a lot of interest as a transparent conductive electrode material. It has been great material owing to the ease of nanowire manufacture, scalable solution. They possess high conductivity and mechanical ductility. They can be utilized in a network form like SWCNTs, therefore

SWCNTs and AgNWs can be coated together on several surfaces homogeneously. In this thesis, AgNWs were also added to SWCNT solution in order to improve conductivity. The fabricated AgNW-SWCNT thin films were characterized by SEM and UV-vis spectrophotometer. Sheet resistances of the films deposited via vacuum filtration were also determined. It was found that the sheet resistance values decreased significantly to 95 Ω/sq.

TRANSPARAN VE İLETKEN TEK DUVARLI KARBON NANOTÜP İNCE FİLMLERİN HAZIRLANMASI

ÖZET

Karbon nanotüpler, günümüzde nano teknolojinin vazgeçilmez unsurlarından olup yoğun olarak araştırılan malzemelerdir. Grafit plakasının kırvrılarak elde edilen silindir şeklindeki bu malzemelerin çapları birkaç nanometreyken uzunlukları milimetrelerle ifade edilebilir. Çaplarının milyonlarca katı uzunluklara ulaşabilen karbon nanotüpler, mekanik, kimyasal, ısıl ve elektriksel özelliklerinin çok iyi olmasıyla birlikte birçok farklı potansiyel uygulama için umut vaat eden eşsiz bir malzeme olmaktadır. Geometrilerine bağlı olarak yarıiletken ve metalik özellik gösterirler. Hiçbir katkılama olmaksızın nanotüplerin geometrik parametrelerinin değiştirilmesiyle elektronik özellikleri de değiştirilebilir. Karbon nanotüplerin çok yönlü özellikleri, onları çeşitli geçirgen ve iletken optoelektronik aygıtların kullanımı için uygun hale getirir. Geçirgen ve iletken elektrotlar, güneş pilleri, dokunmatik ekranlar, ışık yayan diyotlar ve birçok optoelektronik aygıtlarda kullanılmaktadırlar.

Yaygın olarak kullanılan geçirgen elektrot, indiyum kalay oksit (ITO)'tir. Ancak, ITO kaplı camlar sadece pahalı değil, mekanik olarak da kırılgandırlar. Aktif bir malzeme olan ITO, aşındırıcı ya da organic bir malzemeyle temas etmesi sonucu kimyasal reaksiyona da girebilir. Ayrıca, sert ve pürüzlü yüzeye sahip olduklarından başka malzemelerle kaplanmaları gerekir. Daha da önemlisi, ITO'nun iletkenliğinin düşük olması güneş pili dolum faktörünü düşürmektedir. Son yıllarda, ITO yerine kullanılabilecek elektrot malzemeleri konusunda çeşitli çalışmalar bulunmaktadır. Gümüş nanoparçacıklar, nanoteller, grafen ve karbon nanotüpler bu malzemeler arasındadır. Karbon nanotüpler; optik geçirgenlikleri, elektriksel ve esneklik gibi eşsiz özellikleri ile, ITO'nun yerine kullanılabilecek çok iyi bir alternatiftir. Ayrıca, tek duvarlı karbon nanotüp ince filmlerin kaplama sürecinde vakum sistemine ihtiyaç yoktur ve çözelti temelli kaplama yöntemleriyle düşük sıcaklıklarda çeşitli altlıklar üzerine geniş alanlara uygulanabilmektedir. Püskürtme ve dönel kaplama teknikleri, geniş alan uygulamalar için uygun kaplama yöntemleridir. Geçirgen elektrot uygulamalarında da tek duvarlı karbon nanotüp ince filmler, pratik püskürtme ve dönel kaplama yöntemleriyle kolaylıkla oluşturulabilir.

Kaplama aşamasından önce homojen karbon nanotüp çözeltisi elde etmek oldukça önemlidir. Bu amaçla, çeşitli çözücüler ve yüzey aktif maddeler kullanılmaktadır, ancak bu maddelerin avantajları olduğu kadar dezavantajları da vardır. Kaplama sonrası bu malzemeleri film yüzeyinden ayırmak için ilave işlemler uygulanmaktadır. Çözücü olarak sıkça kullanılan n-metil pirolidon (NMP) ve di metil formamid (DMF) toksik maddeler olup, özellikle DMF kansere sebep olmaktadır.

Yüzey aktif maddeler ise temel olarak suyu seven ve sevmeyen kısımlardan oluşur. Bu moleküllerin suyu sevmeyen uçları karbon nanotüplere tutunurken suyu seven uçları da nano tüpleri birbirinden uzaklaştırarak su içerisinde homojen olarak

dağılmasını sağlarlar. Suyu seven kısımlar anyonik, katyonik veya iyonik olmayan bir yapıda olabilir. Özellikle iyonik yapıda olanlar suda hızla iyonlarına ayrışarak karbon nanotüplerin daha fazla dağılmasını sağlayabilirler. Karbon nanotüpleri birbirinden ayırmak için en çok kullanılan yüzey aktif maddeler sodyum dodesil sülfat (SDS) ve triton'dur. SDS iyonik, triton ise iyonik olmayan yüzey aktif malzemelere örnektir. Bunların dışında, iyonik yüzey aktif maddelere örnek olarak sodyum dodesil benzen sülfonat (SDBS), sodyum diizopropil naftalin sülfonat (SDNS), hekzadesil trimetil amonyum bromit (CTAB) gösterilebilir. Bu çalışmada, yüzey aktif madde olarak yaygın kullanılan sodyum dodesil sülfat (SDS) ve triton seçilmiş ve çözücü olarak ilave işlemleri azaltmak için distile su kullanılmıştır. Homojen CNT dağılımı SDS ile elde edilmiştir.

Homojen CNT dağılımını, çözücü ve yüzey aktif madde tipi dışında CNT yoğunluğu, karıştırma tekniği, hızı, ve süresi de etkilemektedir. CNT yoğunluğunun bir başka deyişle CNT miktarının yüksek olması karışmalarına dolayısıyla geçirgenliğin azalmasına ve yüzey direncinin artmasına; düşük olması ise iletkenliğin azalmasına sebep olmaktadır. Bu nedenle, en uygun CNT yoğunluğu belirlenmelidir. Ayrıca, karıştırma tekniğine göre uygun güç ve sürede karıştırma işlemi yapılmalıdır. Karıştırıcının düşük güçte olması ya da yeterli süre uygulanmaması karbon nanotüplerin karışmamasına, yüksek güçte uzun süre karıştırılmaları ise karbon nanotüplerin zarar görmelerine sebep olmaktadır. Her iki durumda da yüzey dirençleri artmaktadır.

Transparan ve iletken elektrotlarda, yüzey direncinin yanı sıra geçirgenlik de önemli bir özelliktir. Özellikle, dokunmatik yüzeylerde ve sıvı kristal ekranlarda bu özellik daha da önem arzetmektedir. Yüksek geçirgenlik için birbirine karışan karbon nanotüpleri santrifüj ile çözeltiden uzaklaştırmak gerekir. Böylece, hem geçirgenlik uygun seviyelere ulaşır, hem de iletkenliği engelleyen karbon nanotüp kümeleri yok edilmiş olur. Yeterli sonuçlar elde edilememişse ikinci bir karıştırma işlemi ve santrifüj gerekebilir.

Transparan ince film yüzeyinde, karbon nanotüpler rastgele dağılmış ağ şeklinde bir yapı oluşturmaktadır. Bu yapının iki önemli özelliği, yüzey direnci ve optik geçirgenliktir. Her iki özellik de film kalınlığına bağlı olarak değişebilir. Çoğu uygulamalarda yüksek geçirgenlik ile düşük yüzey direnci gereklidir. Ancak bazı özel uygulamalarda bu gereksinimden uzaklaşılabilmektedir. Genel olarak istenen geçirgenlik elde edildikten sonra yüzey direncinin düşürülebilmesi için asit ile muamele, ısıl işlem gibi çeşitli yöntemler uygulanmaktadır. Asit ile muamele, kullanılan yüzey aktif maddeleri yüzey üzerinden uzaklaştırır. Bu işlemle, kaplama sırasında yeterince temizlenemeyen ve karbon nanotüplerin iletkenliğini azaltan yüzey aktif maddeler film üzerinden temizlenmiş olur. Asit uygulamasında, asit derişimine dikkat edilmelidir. Çünkü, güçlü asit yüzey aktif madde ile birlikte karbon nanotüpleri de yüzeyden tamamen çıkarabilmektedir. Kaplama sonrası uygulanan bir diğer işlem ise, ısıl işlemdir. Bu yöntemde, yüzey aktif maddelerin yanma sıcaklıkları karbon nanotüplerden daha düşük olduğu için, yeteri kadar ısı uygulanarak yüzey aktif maddelerin yanması sağlanmaktadır.

CNT'ler gibi gümüş nanoteller de son yıllarda oldukça ilgi çeken nano malzemelerdir. Üretim kolaylığı, yüksek iletkenlik, mekanik dayanıklılık gibi üstün özelliklerinden dolayı uygun transparan iletken elektrot malzemesi olarak görülebilir. Gümüş nanoteller de CNT'ler gibi çözelti temelli kaplamalarda kullanılmak üzere çözelti içerisinde ve kaplanan yüzey üzerinde ağ şeklinde dağıtılabilirler. Bu nedenle, CNT'ler ve gümüş nanoteller çeşitli yüzeylere homojen bir şekilde kaplanabilirler.

Son yıllarda yapılan çalışmalarda, sadece gümüş nanotel ya da CNT kullanılması yerine her iki malzemenin birlikte kullanılması ile daha verimli sonuçlar elde edildiği görülmüştür.

Tez çalışması kapsamında, tek duvarlı karbon nanotüpler kullanılarak geçirgen elektrot üretilmiştir. Ilk olarak, tek duvarlı karbon nanotüpler, kimyasal buhar birikimi yöntemine göre demir katalizörü ve asetilen gazı kullanılarak 800 °C'de sentezlenmisler ve 3M HNO_3 ile saflaştırılmışlardır (% 98.39). Tek duvarlı karbon nanotüplerin cam yüzey üzerine kaplanmasında, vakum ile süzme ve sprey kaplama yöntemleri uygulanmıştır. Homojen karbon nanotüp çözeltileri hazırlamak amacıyla çeşitli dağıtıcı yüzey aktif malzemeler kullanılmıştır. Elde edilen ince filmler karakterize edilerek farklı kaplama koşullarının (karbon nanotüp yoğunluğu, yüzey aktif madde çeşidi ve karıştırma hızı) optoelektronik özelliklerine etkisi incelenmiştir. Karbon nanotüp çözeltisinin homojen dağılımı için ultrasonik banyo ve homojenizatör kullanılmıştır. Ayrıca, ince filmlerin elektriksel özelliklerini geliştirmek için asitle (HNO_3) muamele ve ısıl işlem uygulanmıştır. Asitle muamele ve ısıl işlem sonuçları karşılaştırıldığında, ince film optoelektronik özelliklerini geliştirmek için ısıl işlemin daha etkili bir yöntem olduğu görülmüştür. Üretilen tek duvarlı karbon nanotüp ince filmler, taramalı elektron mikroskobu ve UV-vis spektrofotometre ile karakterize edilmiştir. İki uçlu direnç ölçüm cihazı ile farklı parametrelerle üretilen ince filmlerin yüzey dirençleri tespit edilmiş ve karşılaştırılmıştır. Ayrıca, iletkenliği artırmak için tek duvarlı karbon nanotüplere gümüş nanoteller de ilave edilmiştir. Elde edilen ince filmlerin yüzey dirençlerinin 95 Ω/□'ye kadar düştüğü belirlenmiştir.

1. INTRODUCTION

In the last decade due to the demand of last generation high technology materials, there is a great interest in nanotechnology [1]. Nanotechnology aims to product smaller, cheaper, lighter, faster device with more functionality and less raw material. Therefore, nanotechnology deals with materials having a size of 1-100 nanometer (nm). The properties of the materials change upon their size. When the nanomaterials are considered, surface behavior of the material is more dominant than the behavior of the overall material and they can be implicated to many fields such as electronics, chemicals, and biotechnology

The identification of the structure of fullerenes in 1985 by Kroto and his team was a breakthrough in nanotechnology [2]. The discovery of multi walled carbon nanotubes (MWCNT) in 1991 and single wall nanotubes followed it in 1993 by Lijima [3,4]. Thereafter the highly intensified research into the science of nanotechnology started due to superior mechanical strength, electronic properties, large surface area, and high aspect ratio of CNTs. Therefore, they have many applications in different fields such as transparent and conductive electrodes.

Transparent electrodes are being utilized several optoelectronic devices. These devices must be thin, lightweight and highly conductive. Transparent conductive films are most commonly prepared using ITO in electronic and optoelectronic devices [5]. ITO exhibits a transparency of >70% and a sheet resistance of 10 – 30 Ω/sq [6]. However, researchers began searching for alternatives to ITO because of the brittle properties and high cost. SWCNT thin films can be preferred as an alternative to ITO due to cost effective, flexible and conductive properties. In addition, SWCNT thin films coating processes does not need a vacuum system that can be applied at low temperatures. With regard to this information, the purpose of this study is to prepare SWCNT thin films which are replaced by ITO and enhance optoelectronic properties.

Fabrication of SWCNT thin films can be done by direct growth or solution based deposition techniques such as vacuum filtration, spin coating, dip coating or spray

coating. Solution based deposition techniques are cheaper and applicable over large areas and various substrates. However, those deposition techniques require homogeneous SWCNT dispersions. SWCNTs have large aspect ratio; thus, they can easily agglomerate in the form of cylindrical bundles under van der Waals forces. In order to disperse SWCNTs, anionic, cationic and non-ionic surfactants or organic solvents can be used. These surfactants provide an electrostatic repulsion at the outer surface areas of the SWCNTs and keep them apart from each other. It is important to utilize an effective and nondestructive surfactant at the same time. Removal of the surfactant from the deposited SWCNT thin films is also a critical point, which is directly proportional to the improvement in the quality of the optoelectronic properties of the thin films. Dispersion process includes sonication steps for surfactant aided SWCNT solutions. Sonication activates the unzipping behavior of the SWCNT bundles. However, sonication type, time and power can damage and shorten SWCNTs due to heat generation. Optimizations of sonication and dispersion parameters directly affect the stability of the dispersion and SWCNT thin film quality.

Optoelectronic properties of the SWCNT thin films can be improved by functionalization. Acid functionalization is a very common post deposition technique, which removes the residual surfactant from the SWCNT side walls. Especially, nitric acid (HNO_3) treatment increases the electrical conductivity of the SWCNT thin films. Thionyl chloride ($SOCl_2$) can also be utilized for reducing the sheet resistance of the thin films.

Chapter 2 presents the properties of CNTs from different aspects in details. Structure, types, properties and potential applications of CNTs were given to understand this high technology material.

Chapter 3 investigates SWCNT thin film fabrication process from many viewpoints including dispersion, deposition and post-deposition treatments in detail. Optoelectronic properties of the SWCNT thin films were given and compared for different SWCNT densities. Effect of the sonication types and different surfactants were discussed. Post deposition acid treatment and heat treatment were compared.

Chapter 4 presents the experimental studies performed at this work. It includes CNT synthesis, thin film fabrications and characterizations.

Chapter 5 offers the results of CNT synthesis, thin film preparation and characterization. It includes evaluation of thin films prepared by using vacuum filtration and spray coating methods at different conditions.

The overall results and recommendations for this study are given in Chapter 6.

2. CARBON NANOTUBES

Since the discovery of carbon nanotubes by Iijima in 1991, it has been used in number of studies The cause of these studies can be understood by the unique structure and properties of carbon nanotubes. A carbon nanotube occur graphene layer that is properly rolling in nanoscale. Therefore, planar sp^2 bonding of graphite is quite important factor for carbon nanotube. Ideally, a nanotube is hexagonal network which consist of carbon atoms and it has perfect crystal structure [1–3].

CNTs are mainly classified in two categories, SWCNTs and MWCNTs. SWCNTs can be described as the fundamental structural unit of nanotube with one atom thick wall Figure 2.1. The structure of SWCNT is explained in a one dimensional unit cell formed by rolling an infinite sheet of graphene having a diameter size distribution of 1-2 nm [10]. However with zeolite substrate it could be manages to synthesize nanotubes having diameters of 0.4 nm [7]. When compared to MWCNTs, SWCNTs have an elastic structure that allows them to be straight, bended.

Figure 2.1: Drawing of SWCNT [1].

MWCNTs have the coaxial structure of two or more nested tubes as shown in Figure 2.2 [11]. Typically, diameter of these tubes is larger than 2 nm inside and smaller than 100 nm outside. However, the smallest inmost tube in MWCNT was found to be

0.4 nm whereas the outmost tube in MWCNT can be hundreds of nm [12]. The distance between the outer and the inner walls were calculated to be 0.339 nm and it is measured via x-ray diffraction and transmission electron microscope as 0.34 – 0.39 [13-16]. As the measured distances are larger than the distances between the plates of graphite that is 0.334 nm, it is claimed that tangles and twists can be observed in MWCNTs.

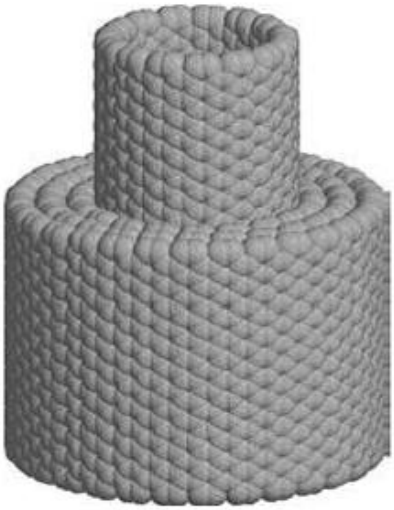

Figure 2.2: Drawing of MWCNT [5].

2.1 Crystal Structure of Carbon Nanotubes

Carbon nanotubes can be classified as arm chair, zigzag and chiral according to their crystal structures. There are some basic terms to describe crystal structure of CNTs. Figure 2.3 shows one sheet of graphene that is rolled to form a single nanotube with chiral vector (C_h) and primitive translation vector (T) of the tube [17].

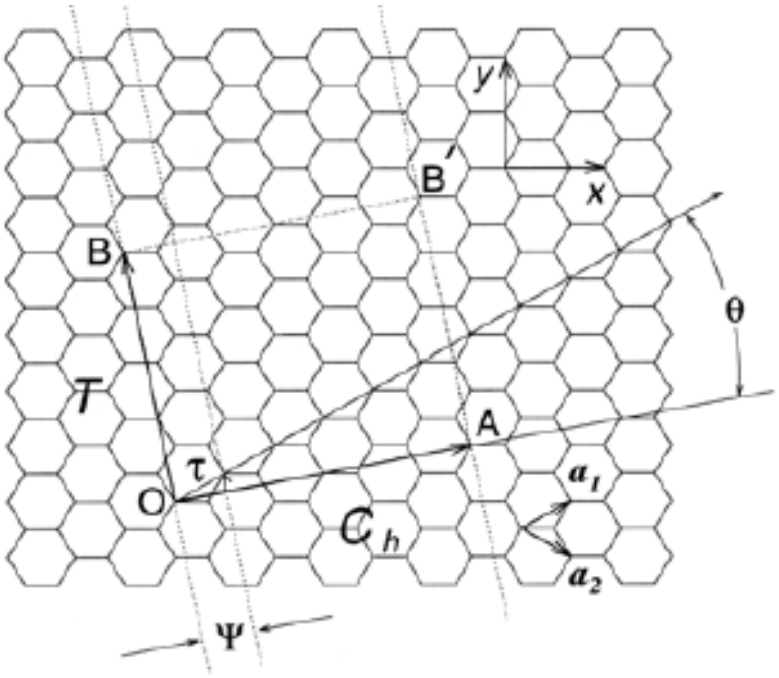

Figure 2.3: Unit cell of a CNT [11].

To express the circumference of a carbon nanotube chiral vector that is defined by two integers m and n and unit vectors of a graphene sheet is used:

$$c_h = n.a_1 + m.a_2 = (n+m) \qquad \textbf{(2.1)}$$

In the figure the chiral vector connects two lattice points A and O having an angle of θ so called chiral angle with the zigzag direction of (n,0). An infinite strip perpendicular to chiral vector is cut through these two points. Diameter of the carbon nanotube and the chiral angle can be found depending on (n,m) values:

$$d_t = \frac{1}{\pi}(\sqrt{n^2 + m^2 + n.m}).a \qquad \textbf{(2.2)}$$

$$\sin\theta = \frac{\sqrt{3}.m}{2\sqrt{n^2 + m^2 + n.m}} \qquad \textbf{(2.3)}$$

When a graphene sheet rolled with a chiral angle of θ, a (n,m) carbon nanotube is formed. There are different types of CNT depending on (n,m) values as shown in Figure 2.4 [17]. (n,0) nanotube with a chiral angle of 0° is called zigzag nanotube, (n,n) with a chiral angle of 30° is called armchair nanotube and if n is not equal to m

and chiral angle is between 0° and 30° then it is called chiral nanotube. Different structural parameters of CNTs can be seen in Table 2.1 [17].

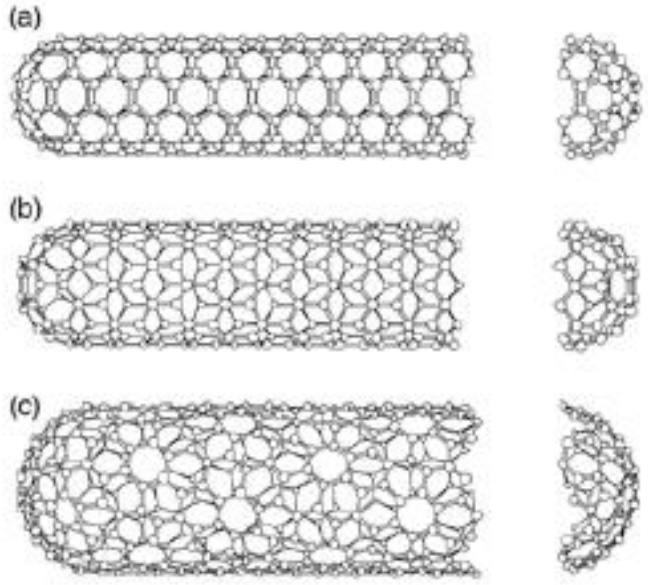

Figure 2.4: a) armchair (n,n) b) zizag (n,0) c) chiral (n,m) nanotubes [11].

Table 2.1: Structural parameters of CNTs [12].

symbol	name	formula	value
a	length of unit vector	$a = \sqrt{3}a_{C-C} = 2.49$ Å,	$a_{C-C} = 1.44$ Å
$\mathbf{a}_1$,$\mathbf{a}_2$	unit vectors	$\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a$, $\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$	x, y coordinate
$\mathbf{b}_1$, $\mathbf{b}_2$	reciprocal lattice vectors	$\left(\frac{1}{\sqrt{3}}, 1\right)\frac{2\pi}{a}$, $\left(\frac{1}{\sqrt{3}}, -1\right)\frac{2\pi}{a}$	x, y coordinate
$\mathbf{C}_h$	chiral vector	$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m), \quad (0 \le \lvert m \rvert \le n)$	
L	length of $\mathbf{C}_h$	$L = \lvert\mathbf{C}_h\rvert = a\sqrt{n^2 + m^2 + nm}$	
d_t	diameter	$d_t = L/\pi$	
θ	chiral angle	$\sin\theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}$	$0 \le \lvert\theta\rvert \le \frac{\pi}{6}$
		$\cos\theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$, $\tan\theta = \frac{\sqrt{3}m}{2n + m}$	
d	$\gcd(n,m)$[b]		
d_R	$\gcd(2n + m, 2m + n)$[b]	$d_R = \begin{cases} d & \text{if } (n - m) \text{ is not multiple of } 3d \\ 3d & \text{if } (n - m) \text{ is multiple of } 3d \end{cases}$	
$\mathbf{T}$	translational vector	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 \equiv (t_1, t_2)$	$\gcd(t_1, t_2) = 1$[b]
		$t_1 = \frac{2m + n}{d_R}$, $t_2 = -\frac{2n + m}{d_R}$	
T	length of $\mathbf{T}$	$T = \lvert\mathbf{T}\rvert = \frac{\sqrt{3}L}{d_R}$	
N	Number of hexagons in the nanotube unit cell.	$N = \frac{2(n^2 + m^2 + nm)}{d_R}$	
$\mathbf{R}$	symmetry vector	$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 \equiv (p, q)$	$\gcd(p, q) = 1$[b]
		$t_1 q - t_2 p = 1, \quad (0 < mp - nq \le N)$	
τ	pitch of $\mathbf{R}$	$\tau = \frac{(mp - nq)T}{N} = \frac{MT}{N}$	
ψ	rotation angle of $\mathbf{R}$	$\psi = \frac{2\pi}{N}$	in radians
M	number of $\mathbf{T}$ in $N\mathbf{R}$.	$N\mathbf{R} = \mathbf{C}_h + M\mathbf{T}$	

[a] In this table n, m, t_1, t_2, p, q are integers and d, d_R N and M are integer functions of these integers.

[b] $\gcd(n, m)$ denotes the greatest common divisor of the two integers n and m.

2.2 Properties of Carbon Nanotubes

As one class of nanostructured materials, CNT have been receiving much attention due to their remarkable mechanical properties and unique electronic properties as well as the high thermal and chemical stability and excellent heat conduction [12].

2.2.1 Mechanical properties of carbon nanotubes

The remarkable mechanical properties of CNTs are closely related to carbon-carbon bonds. σ bonding is known to be strongest in nature and as nanotube is structured with all σ bonds. Thus nanotube is regarded as fiber with the strength in its tube axis. Theoretical and experimental studies show elastic modulus and tensile strength of CNTs are changing in the range of 1000 and tens of GPa respectively [18]. It is known that CNTs have the highest elastic modulus among other materials including graphite [19]. In experimental studies, Treacy et al. found the Young's modulus of MWCNT in a wide range of 0.4-4.15 TPa with an average of 1.8 TPa in a transmission electron microscope [20]. Thus, CNTs can resist to any physical force applied to its walls. Table 2.2 summarizes the calculated Young's modulus and tensile strength of CNTs [12].

Table 2.2: Mechanical properties of nanotubes.

	Young's Modulus	Tensile Strength	Density
	(GPa)	(GPa)	(g/cm^3)
MWCNT	1200	~150	2.6
SWCNT	1054	75	1.3
SWCNT bundle	563	~150	1.3
Graphite (in-plane)	350	2.5	2.6
Steel	208	0.4	7.8

Various types of defect-free nanotubes are generally stronger than graphite. This is a result of increase in the axial component of σ bonding when graphite sheet is rolled to form SWCNT. Young's modulus is dependent on the tube diameter but independent of tube chirality. When the tube is large its Young's modulus is approaching to graphite but as the tube gets smaller it is mechanically stable. When different diameters of SWCNT form a MWCNT, the Young's modulus will be

higher than SWCNT as a result of Van der Waals force [7]. However, when SWCNTs form bundles the Young's modulus will be smaller than a single SWCNT due to weak Van der Waals forces.

Elastic property of CNTs is also remarkable. Majority of the hard materials fail with a strain of 1% as result of defects and dislocations. However, both theoretical and experimental studies concluded that CNTs can stand up to 15% tensile strain before fracture [21]. Thus the tensile strength could be 150 GPa with a Young's modulus of 1TPa. Salvetat et al. concluded that the elastic and shear modulus of a SWCNT are 1 TPa and 1 GPa respectively [22]. As a result of their flexible structure CNTs can be bent repeatedly up to 90° without being broken or damaged.

2.2.2 Electrical properties of carbon nanotubes

Depending on the chirality, nanotubes can be either metal or semiconductor even though they have the same diameter [10]. When a graphite sheet is rolled to form CNT not only the carbon atoms are ordered around the circular structure but also quantum mechanical wave functions of the electrons are ordered accordingly. The electrons are bounded in radial directions by the single layered graphite sheet. There exist periodical boundary conditions around the circle of the nanotube. If there are ten hexagons around nanotube then the eleventh hexagon fits to first hexagon. As a result of the quantum boundaries the electrons are effective only along the nanotube axis enabling to determine the wave vectors. Thus small diameter nanotubes are either metallic or semiconductors.

According to electrical properties, nanotubes can be classified as large gap, tiny gap and zero gap nanotubes. Theoretical calculations show that electrical properties of nanotubes depend on geometric structure. Graphene is a zero gap semiconductor, according to the theory CNT can be metals or semiconductors having different energy gaps depending on diameter and helicity of nanotubes. As the nanotube radius R increases the band gap of large gap and tiny gap nanotubes decrease with 1/R and $1/R^2$ dependence, respectively [23-25]. The electrical properties of SWCNTs depend on n and m values:

If n=m forming armchair nanotube is metallic,

If n-m=3k; k € Z, k≠0 the nanotube it is tiny-gap semiconductor that is metallic at room temperature,

If n-m= 3k ± 1; k € Z, k≠0 large-gap semiconductors.

Experimental studies performed by applying electrical field to nanotubes are proving the theoretical calculations. Experimental studies was observed that SWCNT with a diameter of 0.4 nm became conductive at 20 K [26].

In the measurements of SWCNTs, it was observed that each nanotube acts individual conductivity and the resistivity is at 300 K is in the range of ~1.2×10^{-4} to 5.1×10^{-6}. SWCNT bundles have metallic behavior with a resistivity of 0.34×10^{-4} to 1.0×10^{-4} whereas copper has a resistivity of 1.7×10^{-6} ohm cm. Briefly the electrical resistivity of CNTs is very close to copper. Metallic nanotubes have remarkable conductivities. Although a CNT bundle can transport a current density of 1×10^{9} A/cm^2 copper wires can transport 1×10^{6} A/cm^2 which is thousand times less than CNTs [27].

2.2.3 Thermal properties of carbon nanotubes

As well as their electrical and mechanical properties CNTs have a reputation for their thermal properties. Nanomaterials are affected by quantum properties. Low temperature, specific heat and the interaction CNTs with each other are utilized for phonon velocity on CNT. Thermal properties of CNTs have been both theoretically and experimentally investigated. Theoretically thermal conductivity of CNTs is better than graphite. In research, thermal conductivity of SWCNTs was measured to be 200 W/mK whereas MWCNTs had an electrical conductivity of 300 W/mK [27]. As result of Fermi level current density, metallic SWCNT is a one dimensional metal. It has a linear electronic thermal capacity at low temperatures. Theoretically MWCNTs are expected to have lower thermal conductivity than graphite which has low thermal conductivity due to weak Van der Waals forces. MWCNTs have only Van der Waals forces between the nanotube layers. Thermal expansion of CNTs is expected to be better than graphite. It was a matter of question whether CNTs would have high thermal conductivity due to high thermal conductivities of diamond and graphite. The thermal conductivity is the ability of material to transport the heat from high temperature region to low temperature region as shown in Formula 2.4 where q is the change of heat in unit time per unit area, k is the thermal conductivity coefficient, and dT/dx is the thermal gradient along the material.

$$q = -k.\frac{dT}{dx} \qquad \textbf{(2.4)}$$

Thermal conductivity of diamond is 1000-2600 W/mK and graphite is 120 W/mK at 100°C. Hone et al. calculated the thermal conductivity of an individual SWCNT as 1800-6000 W/mK at room temperature [28]. However researches, it was found to be 2980 W/mK and 6600 W/mK at room temperature [23, 24]. Thermal conductivity of MWCNTs are in the range of 1800 to 6000 W/mK.

2.2.4 Chemical properties of carbon nanotubes

Due to their small radius, large specific surfaces and σ-π hybridization CNTs have strong sensitivity to chemical interactions. As a result of this fact they are attractive materials for chemical and biological applications [12]. However these properties challenges the characterisation of CNTs and determination their properties.

Reactivity of CNTs are determined by direction of π orbitals and pyramidization of the chemical bonds. Some bonds in CNTs are neither perpendicular nor parallel to the tube axis. Therefore, π orbitals cannot be properly directed which affects the reactivity of the CNT. As the diameter of CNT decreases, the reactivity of CNT increases.

As a result of the chemical stability and perfect structure of the CNTs the carrier mobility at high gate fields may not be affected by processing like in the conventional semiconductor channels. Nonetheless, low scattering, with the strong chemical bonding and extraordinary thermal conductivity, allows CNTs to withstand extremely high current densities up to ~109 A/cm^2 [8].

2.3 Synthesis Methods of Carbon Nanotubes

As CNTs have wide range of applications, the growth techniques which can sustain high purity, and more amount of CNT becomes crucial. CNT synthesis can be achieved by three basic methods. These are arc discharge, laser ablation and chemical vapor deposition (CVD). The details of the CNT synthesis methods are described below.

2.3.1 Arc discharge

Arc discharge is the most common technique for the synthesis of high quality SWCNTs. Both SWCNTs and MWNTs can be synthesized by this method. In 1991 Iijima reported formation of carbon nanotubes with arc discharge method which is previously used for production of fullerenes [3]. The tubes were produced with diameters ranging from 4 to30 nm and having lengths up to 1μm [31].

In arc discharge method as shown in Figure 2.5 a direct current electric arc-discharge in inert gas atmosphere is produced by using two graphite electrodes [4], [31], [32]. The carbon nanotubes grow on the negative end of the carbon electrode that is producing the direct current while Argon as inert gas passes through the system. In arc discharge method a power supply of low voltage (12 to 25 V) and high current (50 to 120 A) is used. Catalyst, Ar:He gas ratio, the distance between the anode and the cathode, the overall gas pressure are the other parameters affecting the quality and the properties (i.e. diameter, yield percent) of CNT synthesized by arc discharge method [33-35].

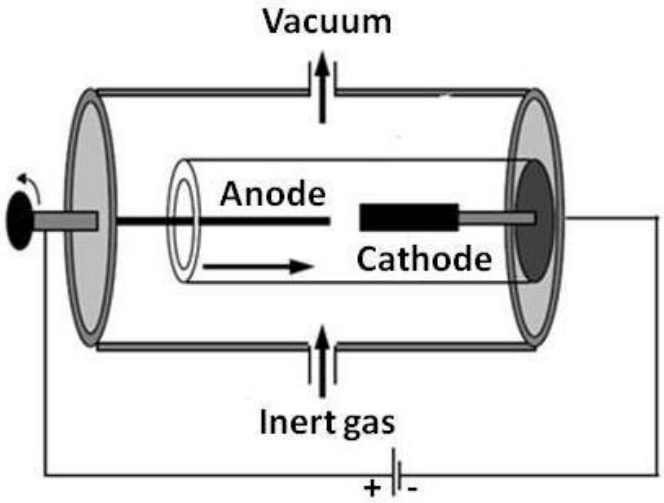

Figure 2.5: Diagram of arc discharge method [26].

In an arc discharge process, CNTs are prepared with a power supply of low voltage and high current. While the positive electrode is consumed in the arc discharge gas atmosphere (i.e. Ar, He) CNT bundles are formed on the negative electrode [36]. Length of MWCNTs produced by arc discharge method are generally around 1μm having a length to diameter ratio (aspect ratio) of 100 to 1000 [37]. As a result of

high aspect ratio and small diameter of the produced MWCNTs they are classified as 1D carbon systems.

It has been reported that in the production of SWCNTs by arc discharge method existence of catalyst (i.e. Fe, Co etc.) is required [27, 33–35]. Many catalyst composition can produce MWCNTs but it is observed that Y:Ni mixture yield up to 90% with an average diameter of 1.2 to 1.4 nm [35].

2.3.2 Laser ablation

Laser ablation method is very similar to arc discharge method as it also uses a metal impregnated carbon source to produce SWCNT and MWCNT [40], [41]. In the laser ablation method, 1.2 at % Co:Ni and 98.8 at% graphite composite is used in an inert atmosphere around 500 Torr of He or Ar in a quartz tube furnace of 1200ºC [8]. Treated to laser light as pulsed or continuously, the nano sized metal particles formed in the vaporized graphite; catalyse the growth of SWCNT and by products. These products are condensed on the cold finger downstream of the source as shown in Figure 2.6 [8]. Smiley group in Rice University achieved the first large scale production of SWCNTs by laser ablation method in 1996 [37]. The production yield of weight varies between 20 to 80% SWCNTs and the tube diameter ranges are 1.0 to 1.6 nm.

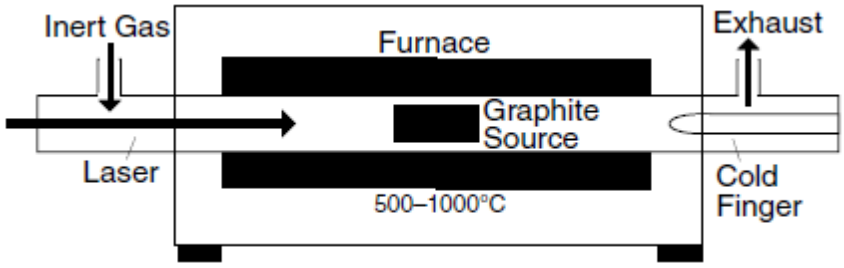

Figure 2.6: Schematic view of laser ablation furnace.

2.3.3 Chemical vapor deposition

Unlike the laser ablation and arc discharge method, thermal synthesis method depends on thermal source to produce CNTs by breaking down the carbon source generally with existence of catalysis [8]. High pressure CO synthesis, flame

synthesis, chemical vapor deposition (CVD), and plasma enhanced chemical vapor deposition (PECVD) synthesis are methods using thermal source to produce CNTs.

CVD method is deposition of a hydrocarbon gas as carbon source (i.e. acetylene, methane etc.) on a metal catalyst (Fe, Co, Ni, Pd etc) at temperatures between 500 and 1200 ºC. CVD has been used for production of nanofibers for long time till Yacaman et.al used it for production of CNT [42]. CVD is preferred for CNT syntheses for high purity and large scale production [8], [43], [44]. CVD which was first reported to produce MWCNTs by Endo et al., can synthesize both SWCNTs and MWCNTs [39]. One of the main challenges in CNT production, which is CVD method with existence of catalysts is maintain mass production and low cost.

CNT production by CVD can be either on a fixed bed or fluidized bed reactor. In fixed bed CVD method as shown in Figure 2.7, the furnace placed horizontal to the ground and the quartz tube is placed in it [18]. The substrate material (MgO, alumina, zeolite etc.) coated with a catalyst (Fe, Co, Ni, Ag, Ti, etc.) is placed in the quartz tube and fed by a carbon source (i.e. hydrocarbons). Generally with existence of an inert gas to maintain continuous gas flow. There are a number of parameters affecting the quality and amount of CNTs synthesized by CVD method.

- Temperature
- Type and amount of the catalyst material
- Type and amount of the substrate material
- Gas flow rate
- Duration of the synthesis
- Diameter of the reactor

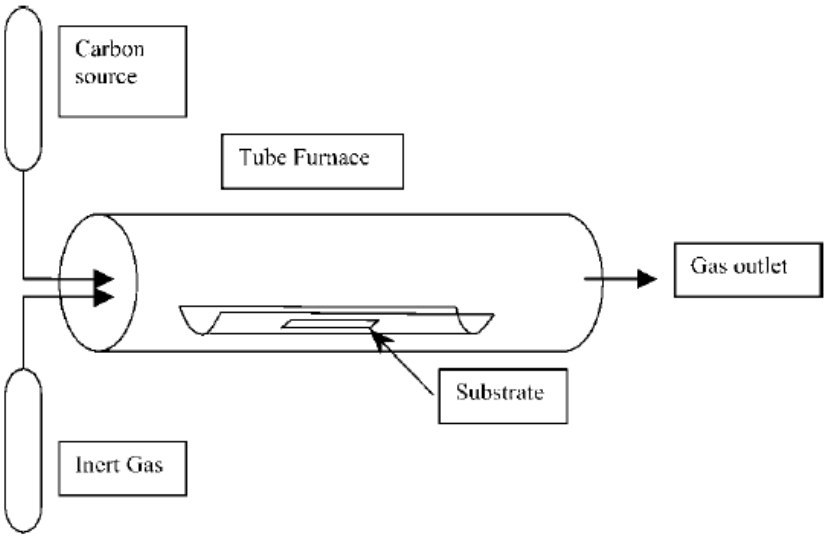

Figure 2.7: Schematic view of fixed bed CVD reactor [12].

In fluidized bed CVD method as the interaction area of the carbon source gases and the catalyst increases with fluidization, large scale production is possible. As shown in Figure 2.8 the furnace is placed vertical to the ground and the quartz reactor is located in it. The substrate & catalyst couple is placed in the hot zone of the furnace, and the gas flow through the reactor is maintained. As the carbon source gas flows through the reactor the catalyst and substrate interacts with the gas and decomposes it for CNT synthesis.

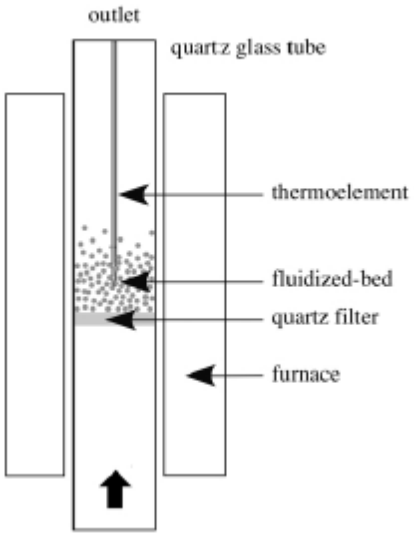

Figure 2.8: Schematic view of fluidized bed CVD reactor.

PECVD method is required for some processes that cannot tolerate temperatures thermal CVD. In CCVD method CNT is synthesis generally achieved above

temperatures of 500°C. However, MWCNT production at 120°C is possible by PECVD method [12]. Plasma can dissociate the hydrocarbon with reactive radicals. Therefore the hydrocarbon is generally fed to the system with another gas such as argon, hydrogen, ammonia [12] to dilute the hydrocarbon.

2.4 Potential Applications of Carbon Nanotubes

CNTs have a wide range of applications regarding to their excellent material properties. The size and the morphology of CNTs affect the type of the application. If the diameter of the CNT is large, it is generally used in energy devices such as, fuel cells, lithium ion batteries and capacitors. Large fibers can also be used as thermal conductors and filler materials in composites. As the diameter of the CNT decreases, CNT can be used as filler in three phase composites. The CNTs in the resin of the composites act as an interconnection between the fibers and enhance the electrical and thermal conductivity of the material. Nanotubes can also be used in field emitters, optical polarizers, energy storage, and medical applications.

The exceptional mechanical properties lead us to two main applications: strengthening of fibers in high performance composites and replacing the carbon fibers, Kevlar and glass fibers as probes in scanning tunneling microscopes (STM) and atomic force microscopy (AFM) [8]. With excellent mechanical properties, CNTs can be used in composites. One of the main problems in composite formation is to achieve good adhesion between the CNTs and the matrix, which requires covalent coupling. In order to achieve these functional groups can be introduced to the walls forming sufficient number of connections to the walls without weakening the stability of the tubes.

CNTs with their polymer composites are used increase the strength of automotive components. These composites CNTs can form semiconductor materials from insulators. It is expected CNTs may replace silicon in transistors of computer processors and rams. CNTs can also be used in chips with their ability to form Van der Waals bonds. Transport measurements on semiconducting nanotubes have shown that a nanotube connected to two metal electrodes has the characteristics of a field-effect transistor [31].

CNTs are also able to store energy with their porous, light structure in addition to wide surface areas. There is a remarkable interest in especially hydrogen storage in CNTs. It is observed that CNTs have ability to store hydrogen up to 10% of their weight. This can be achieved either at high pressure or by electrochemical methods.

In summary CNTs can be used in; composites, frequency selective surfaces, thermal barriers, nanosensors, nanodevices, hydrogen adsorption, magnetic field emitters, membranes, and biological and medical applications.

3. CARBON NANOTUBE THIN FILM FABRICATION

CNT thin films can be fabricated both by high temperature growth processes such as CVD [45], or by post-growth deposition of the nanotube material from solution [46]. The direct growth of nanotubes onto a substrate has several advantages, such as the high purity of material, and the ability to grown vertically or horizontally aligned structures, as shown in Figure 3.1. However, the growth temperatures for CVD processes are typically at least 500°C, which makes these processes incompatible with plastic substrates. Also, the density of the films is difficult to control, and cannot be made to be greater than one monolayer.

As an alternative, several room temperature fabrication processes have been developed, each involving dispersing a nanotube powder into a solution, and deposition of the subsequent solution. The common element in all solubilization and deposition schemes discussed here is that they are all room temperature processes, which ensures compatibility with a variety of surfaces that are used for printed electronics, such as plastics or other polymers. This thesis focuses on CNT thin films, which were fabricated by solution based depositions; namely by vacuum filtration and spray coating methods.

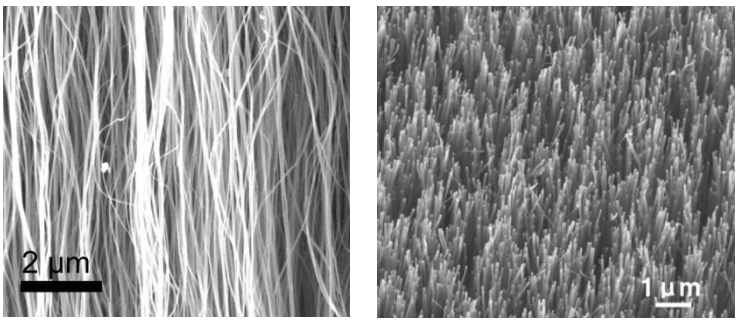

Figure 3.1: Horizontally (a) and vertically (b) aligned nanotubes grown by CVD [47, 48].

3.1 Carbon Nanotube Solution Preparation

The method used to prepare CNT solutions can be generally described in the following processing steps: CNTs are batch synthesized [49], and purified to remove

any residual catalysts, amorphous carbon, and other impurities [50,51]. Then, they are dissolved into solution with the aid of high power sonication. It is known that all current CNT synthesis techniques generate significant amounts of carbonaceous impurities, such as amorphous carbon, graphite sheets, and residual catalysts [31,52]. Without a rigorous purity process to remove the mentioned impurities, subsequent integration of as synthesized CNTs into organic electronics would result in suboptimal performance. After successful purification, it is possible to reach purities of CNTs exceeding 90%. While many variations of purification processes exist, the most common methods include acid purification and subsequent centrifugation as primary steps [53,54]. In this process, CNTs are refluxed in acid (e.g. nitric acid) before room temperature cooling, dilution with DI water, centrifugation, and membrane filtration [53,54]. In addition to removing unwanted residual impurities, acid purification is applied. Because acids are strong oxidants, too harsh of a treatment can result in the conversion of CNTs into carbonaceous impurities [54]. Therefore, much care has to be undertaken during purification as to only dissolve metal catalysts and attack amorphous carbon. After membrane filtration, CNTs are collected and exist in soot powder form in aggregated CNT ropes that can easily be handled for later processing. CNT ropes are bundles of individual CNTs aggregated together due to the high van der Waals forces between CNTs.

With the aid of high power sonication, CNTs in powder form can be dispersed into solvents for future solution processing. Due to the hydrophobic nature of carbon nanotubes, it will not readily disperse into aqueous solutions. Therefore, approaches that are most commonly pursued are: dispersion in organic solvents and surfactant based aqueous dispersion.

Good solubility has been demonstrated in only a limited number of organic solvents, such as *N*-dimethyl formamide (DMF) and dimethyl pyrrolidone (NMP) [55,56]. However, CNT dispersion into these organic solvents typically requires excessive sonication that can lead to considerable mechanical damage and thereby electrical degradation to the nanotubes [57]. In addition, because of down-stream processing, highly flammable and toxic organic solvents such as those mentioned are not desired and as such, water is the preferred solvent.

CNTs are non-polar and thus exhibit hydrophobic behavior in water. Therefore, the aggregated bundles of CNTs do not break up and easily disperse into the aqueous

medium. However, amphiphilic molecules (i.e. molecules containing a hydrophilic head and a hydrophobic tail) such as surfactants can be used to aid in aqueous dissolution. In this approach, the hydrophobic tail readily adsorbs on the surface of CNTs while the hydrophilic head mixes with water (Figure 3.2).

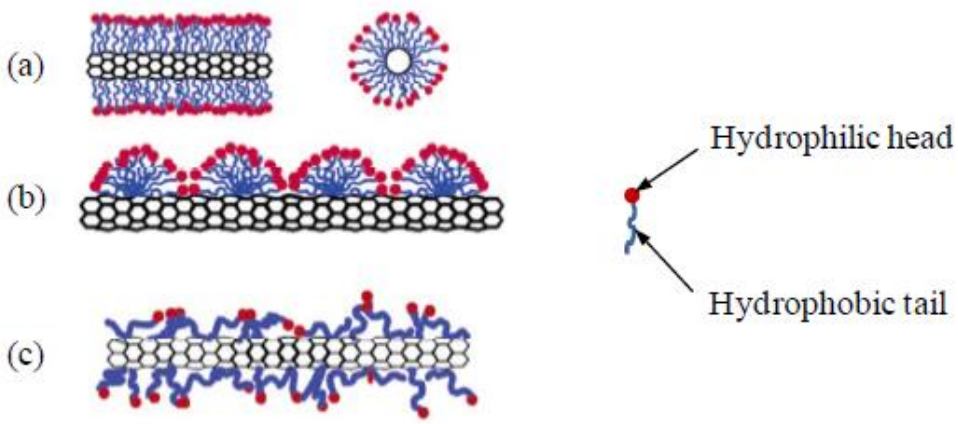

Figure 3.2: a) Cylindrical adsorption, b) hemispherical adsorption and c) random adsorption of surfactants on SWCNT surface [58].

The surfactant also provides sufficient electrostatic repulsion to nearby CNTs to prevent re-aggregation. With the aid of mechanical sonication to break up CNT bundles, the hydrophobic tails of the surfactant can attach to individual CNTs and create stabilized solutions of individual CNTs in water [56]. Figure 3.3 illustrates this process. Common surfactants that have been used to disperse SWCNTs are sodiumdodecylsulfate (SDS) [59], sodium dodecylbenzenesulfonate (SDBS) [60], Triton X [61,62]. The typical surfactant concentration by weight percent is 1% [63, 64]. The photograph of poorly dispersed and well dispersed aqueous based SWCNT solutions are shown in Figure 3.4.

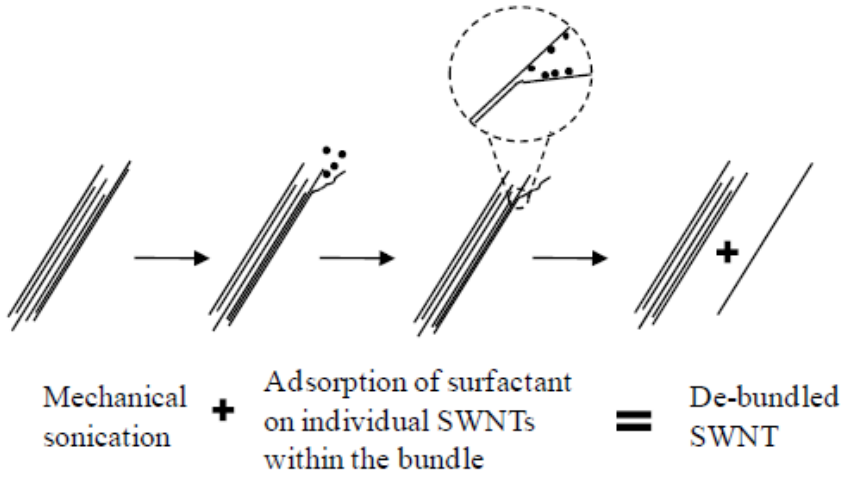

Figure 3.3: Schematic of individual nanotube isolation from bundle via ultrasonication and surfactant adsorption [56].

Figure 3.4: Photograph of poorly dispersed SWCNT solutions (2 images on left) and a well dispersed SWCNT solution (image on right) [65].

Covalent functionalization of CNTs can also assist in aqueous dispersion by creating interactions with the tube surface and surrounding environment. In particular, covalent functionalization of CNTs with carboxylic acids (COOH) has been shown to significantly enhance CNT solubility in water [66, 67]. Refluxing in nitric acid, or sonication in a mixture of sulfuric acid and nitric acid lead to high concentrations of carboxylic acids covalently bonded defects on the sidewalls and the free ends of CNTs (Figure 3.5) [68]. Carboxylic acids are preferentially bonded to the highly reactive defect sites due to large local strains [68]. Surface attached carboxylic acid groups result in the development of a negative electrostatic charge on the CNTs [69]. As a result, the CNTs lose their pristine non-polar characteristics and become more hydrophilic. Also, the net surface charges act as repulsive forces between individual

CNTs to promote debundling and hinder subsequent aggregation [69]. Because CNTs are typically purified using acid reflux, if no further treatment is taken to remove carboxylic acid groups, all purified CNTs will contain a non-negligible amount of acid groups [70]. However, some CNTs manufacturers provide CNTs with enhanced levels of attached carboxylic acid groups by ensuring that functional groups created during acid treatment are retained throughout the purification process.

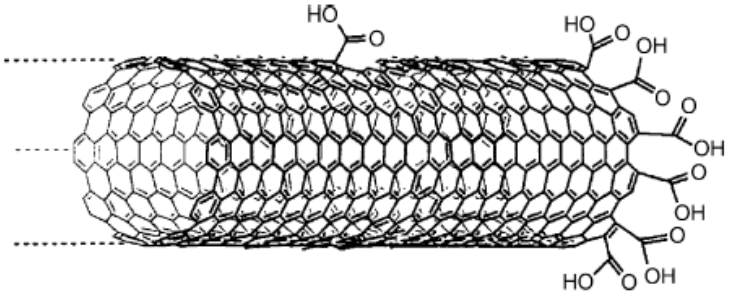

Figure 3.5: Chemical structure of SWCNT with carboxylic groups attached [68].

Dispersion of CNTs in solution is performed with the aid of mechanical separation via sonication. The amount of ultrasonic energy necessary to produce stable solutions of CNTs is dependent on the surfactant/solvent selection, attractive forces between individual CNTs, and the degree of individual CNT to bundles/ropes of CNTs desired. As more energy is added to the solution via sonication, the percentage of individual CNTs increases. However, sonication has been shown to induce mechanical damage to CNTs; therefore, an acceptable compromise must often be met [57]. After initial CNT solutions are prepared via sonication, centrifugation is also used to produce CNT solutions high in individual CNT content and low in non-CNTs impurities [64,71]. Centrifugation has been shown to remove graphitic impurities, catalyst residuals, and large CNT bundles from CNT solutions due to density variations [71].

3.2 Carbon Nanotube Films Processed From Solution

Successful methods to produce randomized CNT networks from solution include spray coating [72], dip coating [61], electrophoretic deposition [73], spin coating [90], and vacuum filtration [59,63]. Achieving a uniform network can be challenging and depends on many parameters like dispersion and CNT solution – substrate interaction. Each of these methods has their own requirements that can be considered

as an advantage or disadvantage. The basic concepts of the deposition techniques above will be discussed in detail. In addition to this information, some major figures of merit, which are used to investigate CNT thin films like optical transmittance and sheet resistance, will also be discussed.

3.3 Deposition Techniques

3.3.1 Dip coating

Dip coating method generally used to produce transparent layer. It is the practical and cost effective technique. Substrate is simply slowly dipped into a pretreated solution and then slowly withdrawn. Finally, coated substrate was dried in ambient conditions. This method yields films of high uniformity and high yield. It is clearly a process that scales to roll to roll manufacturing. It is important that the solvent has low enough surface tension on the substrate that it wets the substrate; if it does not, defects such as repellencies or steaks can occur. On the other hand, solution viscosity, coating speed and drying conditions are important parameters that can affect thin film quality. A schematic of the dip coating process is shown in Figure 3.6.

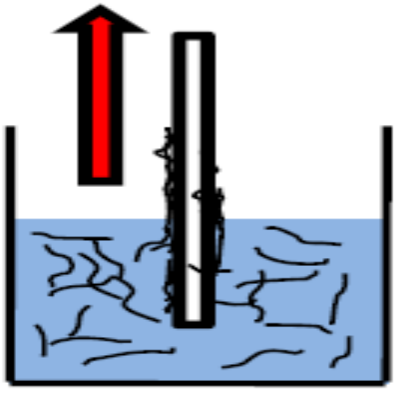

Figure 3.6: Schematic illustration of the dip coating method [61].

3.3.2 Spin coating

Spin coating is a common process used to apply uniform thin films to flat substrates. An excess amount of solution is placed on the substrate that is subsequently rotated at high speeds to produce a centrifugal force that spreads the fluid uniformly over the substrate (Figure 3.7). The film thickness was controlled by the number of times a

spin-coated layer was allowed to dry to have a successive layer spin coated on top of it. The advantage of spin coating is that spreads the solution homogeneously over the substrate. However, this method is not suitable for many CNT thin film applications because of the fact that it requires multiple coating cycles to make a uniform film and it cannot be scaled-up.

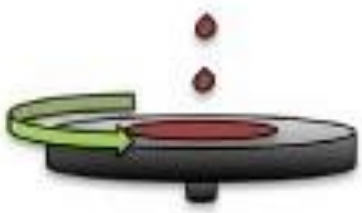

Figure 3.7: Schematic illustration of the spin coating method [74].

3.3.3 Spray coating

Spray coating is the simplest and cheapest deposition technique and the process involves spraying the solution of well dispersed tubes onto a substrate (Figure 3.8). Nanotube solutions are sprayed using an spray brush onto a substrate that is heated. Heating the substrate ensures that the small droplets that hit the surface are evaporated quickly, so the tubes in solution do not have time to aggregate before depositing. Spray coating method has many advantages such as unlike the high vacuum, suitable for large area application. However, stage scan speed, substrate temperature and flow rate should be well optimized before starting the spraying process.

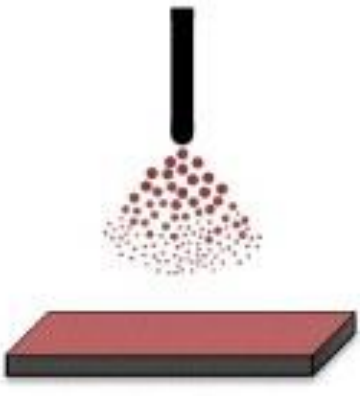

Figure 3.8: Schematic illustration of the spray coating method [74].

3.3.4 Vacuum filtration

Vacuum filtration is the most common method for the fabrication of CNT thin films due to its simplicity and processing consistency. It consist of a vacuum-induced flow of CNT dispersion through the mixed cellulose ester (MCE) filter membranes [59]. As the solution filtered through the membrane, CNTs are collected on the surface. These CNTs form an interconnected network. After filtering the CNT suspension through the porous membrane, the membrane washed with several milliliters of deionized water owing to remove the residual surfactant. The washed membrane is placed on the substrate and dried on hot plate at 70°C under compressive loading to promote adhesion. Transfer of the CNT film onto substrates is completed as a result of the dissolution of MCE membrane in acetone. Multiple acetone baths are applied to remove MCE membranes completely from substrate surface. Film thickness can easily be controlled by the volume of the filtered CNT solution and CNT concentration (Figure 3.9).

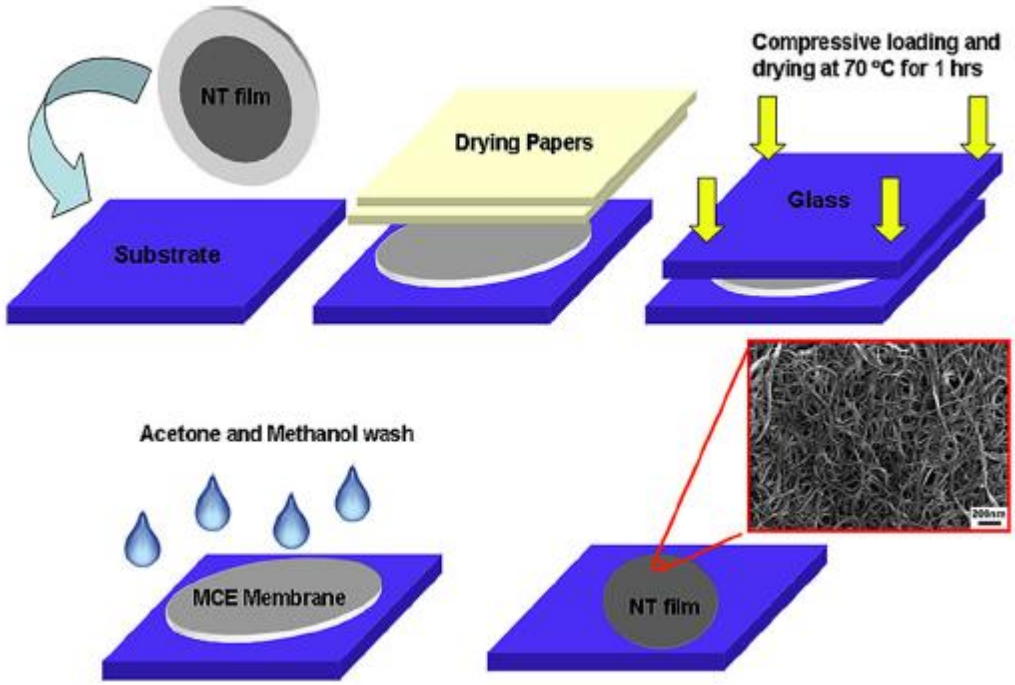

Figure 3.9: Illustration of the SWCNT film transfer via MCE dissolution process. The process proceeds from left to right [75].

3.4 Properties of Carbon Nanotube Thin Films

3.4.1 Sheet resistance of films

The sheet resistance (R_{sh}) of CNT networks is of importance because of its contribution to the resistive power losses in organic devices. R_{sh} is used to characterize the two-dimensional electrical properties of the conductor. This property assumes negligible current flow in the direction perpendicular to the plane of the electrical conductor, thereby only describing lateral conduction within the film. It is given in terms of Ω/sq, and is defined as Formula 3.1.

$$R_{sh} = R\frac{W}{L} \tag{3.1}$$

Since surface density is directly proportional to film thickness, R_{sh} should also scale with the inverse of film thickness. An example of this relationship is shown in Figure 3.10 [76].

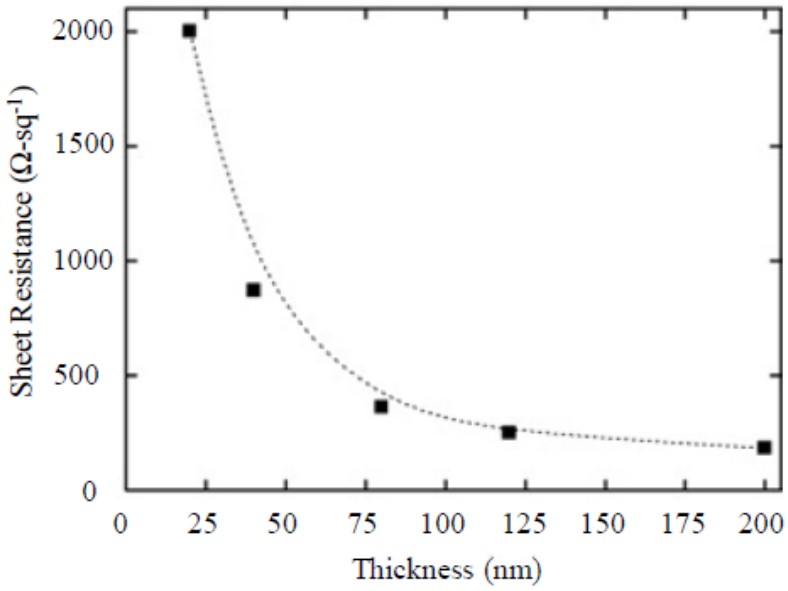

Figure 3.10: R_{sh} as a function of SWCNT film thickness [76].

3.4.2 Optical transmittance of films

When the optoelectronic properties of transparent electrodes are discussed in the literature, the optical transmittance near the visible spectrum is given [77]. The optical transmittance decreases with increasing film thickness. As seen in Figure 3.11, optical losses increase with increasing film thickness due to lower film transmittance while electrical losses decrease with a similar increase in thickness. Therefore, a trade off must be achieved between optical and electrical losses in CNT films. The Figure 3.2 shows the expected performance graphic of SWCNT thin films. Since, a decrease in R_{sh} is most often accompanied with a decrease in transmittance, they are most often combined when presented. In this regard, R_{sh} is often quoted with a given transmittance at 550 nm. Since 80% transmittance at 550 nm is often viewed as a standard benchmark transmission that CNTs transparent electrodes must meet or exceed to be a viable replacement for ITO, R_{sh} is often presented with transmittance $\geq$ 70% [63,78]. State of the art optoelectronic values of pristine SWCNT films include R_{sh} of 186 Ω/sq and 129 Ω/sq with transmittances at 550 nm of 86% [78] and 80% [79] respectively. It must be noted that these state of the art values represent by far some of the best optoelectronic values seen in the literature. Typical R_{sh} values with transmittances at 550 nm of 80-85% are in the range of 250 Ω/sq- 400 Ω/sq [80,81], with many R_{sh} values presented on the kΩ/sq range for a similar transmittance [82].

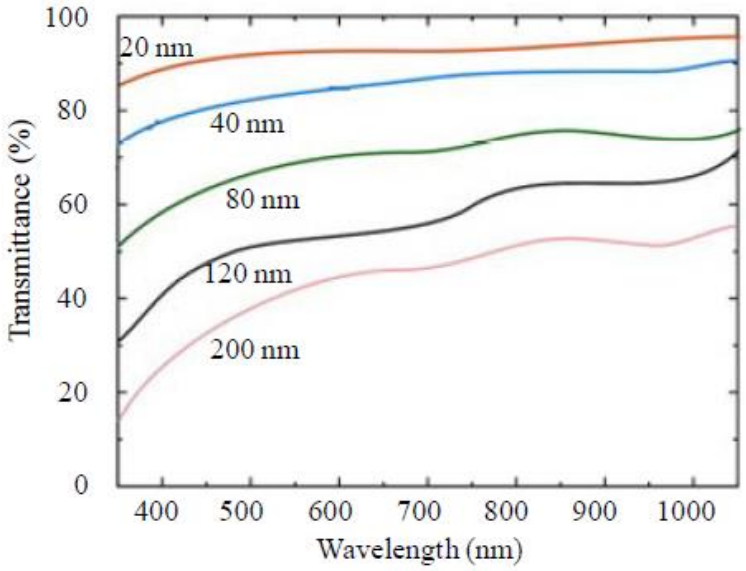

Figure 3.11: Optical transmittance of SWCNT films of several thicknesses [77].

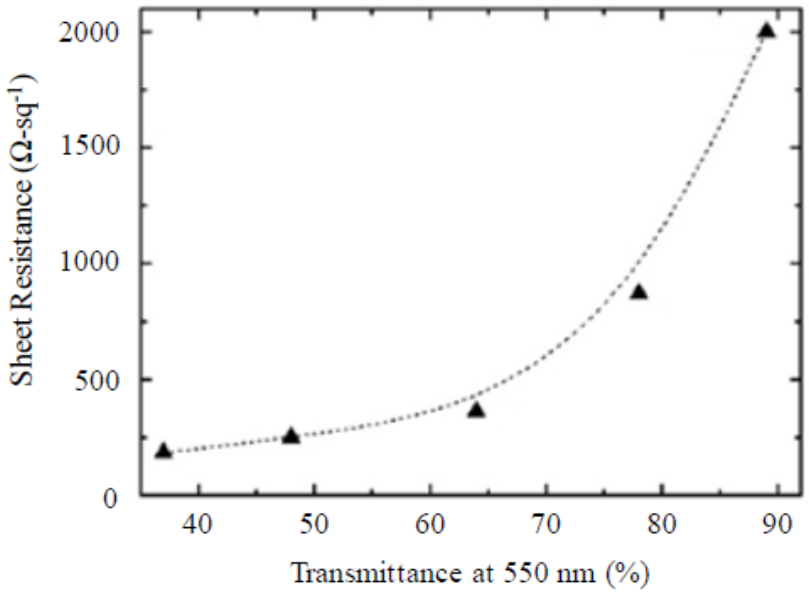

Figure 3.12: Correlation between transparency and R_{sh}. Film transparency represented by transmittance at 520 nm [77].

3.5 Applications of Carbon Nanotube Thin Films

CNTs are unique one dimensional structures, which have shown great capabilities of forming large area, transparent and conductive networks on various substrates. CNT thin films are conformable for numerous applications due to their mechanical flexibility and uniformity such as transparent electrode, thin film transistors, supercapacitors and batteries. In this thesis, the use of CNT thin films for transparent electrode was investigated and discussed in detail.

3.5.1 Transparent electrode

Transparent, conducting materials are widely used in many applications today requiring both transparency in some wavelength range (typically optical wavelengths), as well as high conductivity. The most common materials are the transparent conducting oxides, which are headlined by ITO as the most commonly used transparent conducting oxides. Other alternative materials, however, are emerging as potential candidates as a transparent, conductor, including thin films of conducting polymers, networks of nanowires, patterned metal films, and carbon nanotube networks. The range of applications for these materials is immense, and carbon nanotube networks have demonstrated proof of principle devices in many instances. Some possible applications for nanotubes as a transparent conductor

include: electrodes in liquid crystal displays (LCDs), OLEDs or solar cells, capacitive and resistive touch screens, transparent electromagnetic shielding, invisible security circuits on windows and transparent radio antennas.

When evaluating a material for use as a transparent conductor, there are two important parameters that are evaluated which translate to application performance: the sheet resistance and transmission at a specified wavelength. Typically, most electrode applications demand lower sheet resistance, with higher transmission. The conductivity of nanotube films increases with increasing thickness, nevertheless the transparency of nanotube films decreases.

Aside from the two major parameters of sheet resistance and transparency, there are a countless of other properties that a transparent conductor must have, with different applications each demanding their own unique properties. These properties include items such as the work function, adhesion, thermal stability, surface morphology, hardness, chemical durability, and abrasion resistance.

3.5.2 Literature studies on CNT thin films

Cao et al. have prepared SWCNT thin films used as electrode materials [83]. The successful optoelectronic properties, high transmittance (approximately 70%) and durability were achieved in their studies. Yu et al. [84] deposited CNTs, which were producing by CVD, via wet printing method on glass substrate and they obtained solar cells by layer by layer. 85% transmittance was observed for these CNT thin films. Kitano et al. [85] also deposited thin conductive films of CNTs on glass substrate using a technique based on spray coating for organic solar cells. Transmittance of the fabricated SWCNT thin films was found to be > 80 % at 550 nm. Zhang et al. [68] investigated the chemical doping effect on CNT thin films using thionyl chloride (SOCl2). The film was firstly immersed in SOCl2 for 12 hours followed by drying in nitrogen flow. After this treatment, sheet resistance value decreased by a factor of 2.4 to 160 Ω/sq with a transmittance of 87% at 550 nm. Only a slight decrease in transmittance due to chemical treatment is observed in the wavelength range of 300 – 400 nm. Sierros et al. [86] also prepared the CNT thin films and optical transparency and film thickness were found as 95% and 10 nm, respectively. The study also shows that, durability of CNT transparent electrode was higher (25%) than the most widely used ITO. Besides, the mechanical, electrical and

optical properties of CNTs were examined and determined. Ko et al. [87]synthesized the MWCNTs by CVD method and purified by a treatment with concentrated nitric acid as 99% purity. They prepared MWCNT thin films on PET substrate using a technique based on spray coating. These films exhibited ~77% transmittance at 550 nm even after 500 bending cycles. Shian et al. [88] prepared highly conductive and transparent thin films using SWCNT and silver nanowire (AgNW). Optical transparency of SWCNTs and AgNWs thin films were found as high as 91%. Sibinski et al. [89] compared the thermal properties of CNTs with ITO. They show that the sheet resistance of ITO increases up to 20%, whereas the sheet resistance of CNT decreases down to approximately 4%.

4. EXPERIMENTAL STUDIES

4.1 CNT Thin Film Fabrication

In this study, SWCNTs were firstly synthesized in a fluidized bed CVD system which allows high quality CNT production. The system consists of 3 cm diameter quartz reactor placed in a vertical furnace. The precursor was loaded in the middle of the reactor on a nanoporous silica disc. The high purity Ar gas was purged to obtain an inert atmosphere and then the system was heated to 800 °C. SWCNTs were grown on metal catalyst (Fe-MgO) for reaction time of 30 min with acetylene (C_2H_2) flow. After the synthesis, SWCNTs were purified by nitric acid treatment of 3M HNO_3 for 3 hours at 120 °C to remove metal catalysts.

Vacuum filtration and spray coating methods are utilized for fabricating CNT thin films. Vacuum filtration method requires a subsequent film transfer step as mentioned earlier. Centrifugation, post-deposition acid treatments and heat treatments have also been applied to improve the film quality and optoelectronic properties.

4.1.1 Substrate cleaning

Before starting the experiments, all glasses were cleaned with water and detergent. After washing, they were immersed into nitric acid (HNO_3) solution and then rinse with distilled water to remove the acidic solution from their surfaces. Finally sodium hydroxide (NaOH) solution was utilized and they were rinsed with distilled water again to remove all residuals. In addition, all glasseware used as substrates were sonicated in acetone, isopropil alcohol and deionized (DI) water for 15 minutes each.

4.1.2 Dispersion of CNTs with surfactants

Dispersion of CNT is quite important step for homogeneous thin film. In this work, a simple vacuum filtration and spray coating methods were used to form CNT thin films. Two different surfactants namely SDS and Triton X-405 were selected to disperse the nanotubes. Surfactant assisted SWCNT dispersion was performed in

deionized water. The concentration of SWCNTs was selected as 0.3 mg/ml. SWCNT solution was sonicated for 5 minutes using ultrasonic homogenizer. This sonicator was operated at 60% for an approximate sonication power of 50 Watts. After sonication, the solution was centrifuged at 6000 rpm for 30 minutes. The solution was subsequently and carefully decanted such that only the top 90% of the sample was removed for further processing. The new solution was sonicated again for 5 minutes at 60% power rating and then centrifuged. The second sonication and centrifugation step was used to facilitate SWCNT solutions for further processing free of large bundles and impurities. Afterwards, the top 90% of the centrifuged solution was again decanted.

4.1.3 Dispersion of CNTs with AgNWs

AgNWs were supplied as a suspension in isopropyl alcohol. An aliquote of the AgNW suspension was diluted to 0.1mg/ml with isopropyl alcohol and stored until use. AgNWs having two different concentrations (0.05 and 0.07 mg/ml) were added to 0.3 ml of SWCNT solution having 0.3 mg/ml concentration. AgNW-SWCNT dispersion was performed in 300 ml deionized water by a 30 min bath sonication

4.1.4 Deposition process

4.1.4.1 Vacuum filtration

The well-dispersed supernatant was filtered onto 220 nm MCE membranes (Millipore). After filtration, MCE membrane were washed with 50 ml of distilled water to remove the surfactant residuals. Subsequently the MCE membrane was removed and heated on a hot plate for 10 minutes at 70°C to promote van der Waals adhesion of SWCNTs and SWCNT bundles throughout the nanotube network. Then, the membrane was placed back on the vacuum filtration flask and distilled water was filtered through. The membrane was placed onto glass substrate and the film was quickly placed on the acetone vapor bath to allow the membrane to begin dissolution. The membrane/SWCNT/substrate was placed into 6 sequential acetone baths to dissolve the membrane. Each acetone bath soaking time was approximately 30 minutes.

4.1.4.2 Spray coating

Spray coating is as an alternative deposition technique for large area applications. In this technique, substrates, that had been cleansed, were placed onto a stage capable of moving in two dimensions which was maintained at 100 ^{0}C to avoid fine droplets. SWCNT thin films were spray coated onto 1 x 1 cm² glass substrates. Spraying conditions were optimized to reach the best film performance. The distance between the nozzle and the substrate was 10 cm. Last step was the removal of surfactant. Spray coated samples were dipped into distilled water for 1 h and then dried on a hot plate for 1 h at 80 ^{0}C.

4.1.5 Post-deposition acid treatments

Following the deposition process, SWCNT films on substrates were immersed in 13M HNO_3 for 2 hours and then rinsed thoroughly with distilled water. After they were completely dried with air flow, an additional treatment was subsequently done to improve their conductivities. SWCNT thin films dipped into thionyl chloride ($SOCl_2$) for 2 hours, rinsed and dried with gentle air flow.

4.1.6 Post-deposition heat treatment

Heat treatment was also used instead of acid treatments. Heat treatment has been applied to remove the remnant surfactants in the SWCNT thin films. Following the deposition process, the SWCNT thin films were annealed at 300 ◦C for 3 hours in air atmosphere at a heating rate of 10°C/min.

4.2 Thin Film Characterization Methods

4.2.1 Scanning electron microscope

Homogeneity, density and morphology of the fabricated SWCNT thin films were analyzed by field emission scanning electron microscopy (FEI-Quanta FEG 250). The operating voltage was between 10 and 15 keV. Since the SWCNT thin films were conductive, no further gold/carbon coating was utilized.

4.2.2 Optical transmittance measurements

Transmittance measurements of the SWCNT thin films were performed at room temperature using a UV-Vis spectrometer (T80 UV-Vis) within the range of 300-800 nm wavelengths. A clear bare glass slide was used for the baseline correction.

4.2.3 Sheet resistance measurements

Sheet resistance values of SWNT thin films were measured using a two probe measurement set-up. Keithley 2400 sourcemeter was used as the voltage source. Contact diameters (D) were 0.5 mm and the distance (L) between them was equal to 5 mm. The given formula was used to calculate the sheet resistance (Ω/□) and the measured value from Keithley was put in the equation as resistance (R).

$$R \times \frac{L}{D} = r \qquad \textbf{(4.1)}$$

5. RESULTS AND DISCUSSIONS

5.1 Evalution of SWCNT Synthesis Results

CNT production generally requires existence of a catalyst. The selection of a proper metallic catalyst may affect the morphology amount of the synthesized product, the quality of the product. In this study, the transition metal of iron (Fe) impregnated on MgO powder substrate with weight ratio of 5:100 were used as catalysts. The single wall carbon nanotubes (SWCNTs) were synthesized by catalytic chemical vapor deposition of acetylene (C_2H_2) at 800 °C for 30 minutes. Thermogravimetric analysis (TGA), Raman spectroscopy and transmission electron microscope (TEM) measurements were used for CNT characterization.

TEM images of the synthesized material is given in Figure 5.1. It is evident that the structures synthesized by chemical vapour deposition method are CNTs. The CNTs have diameters between 1.5-5 nm and also are transparent. One possible explanation for the dark parts in both two figures is a result of the impurities within the structures.

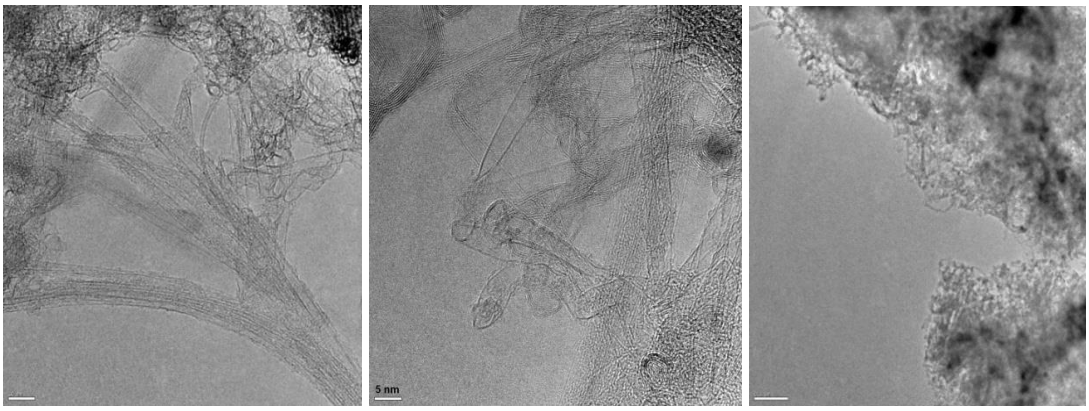

Figure 5.1: TEM images of CNTs synthesized at 800°C.

Figure 5.2 shows Raman spectrum for carbon deposits excited by 633 nm laser. The Raman spectra show the characteristic peaks at 1300 (D band) and 1580 cm^{-1} (G band) for SWCNTs grown on the catalyst. The G and D bands correspond to the degree of graphitization and the defects in CNT structure, respectively. In the Raman

spectra, the ratio of D and G band intensities (I_D/I_G) express the quality of CNTs. The lower the ratio in the spectra refers to the lower content of amorphous carbon and defect formation in the structure. The average ratio of D and G bands of SWCNTs produced on Fe catalyst was around 0.2. The intense and narrow shaped radial breathing mode (RBM) peaks of sample demonstrate that the tube diameter is below 2 nm. The mean diameter of SWCNTs can be calculated using RBM frequency (ω) in Formula 5.1;

$$\omega(cm^{-1}) = A/dia(nm) + B(cm^{-1}) \qquad \textbf{(5.1)}$$

where; A and B are constants (A=234 cm^{-1}; B=10 cm^{-1}) and d is the diameter of SWCNT (28, 29). The mean diameter of the synthesized SWCNTs was calculated as 1.18.

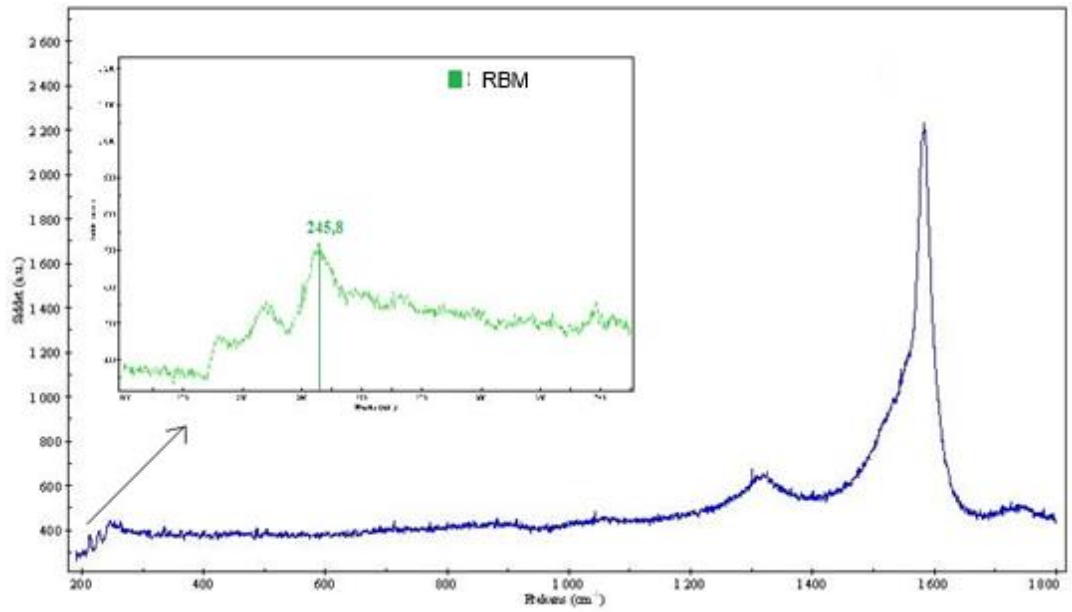

Figure 5.2: Raman spectra of SWCNTs.

Thermogravimetric (TG) analysis is used to characterize the total carbon loading and determine the residual metallic catalyst. The amorphous carbon is completely oxidized at temperatures below 350 °C and graphite burns above 750 °C. The oxidation temperatures of the CNTs depend on the nanotube type and SWCNTs is generally oxidized at the temperatures above 400 °C. In this study, the TG analysis of synthesized SWCNTs was conducted in air atmosphere with a ramp of 5 °C/min between 25 and 800 °C. The yield was defined as the relative weight loss due to the oxidation of the carbon and the result of this analysis is shown in Figure 5.3. As

shown in this figure, carbon nanotube sample has high metal content (about 74%). Moreover, Derivative Thermogravimetric Analysis (DTG) of the sample was accomplished and the result is also shown in Figure 5.3. Since the derivative curves directly reflect the variation in the weight as a function of temperature by occurrence of thermal events (such as the onset of burning), the discussion will focus on these. It can be seen that maximum weight loss of CNTs was occurred at 590°C (DTGmax). Especially, it is observed that DTG curve of the sample has only one peak which belongs to SWCNTs. This is the also evidence of low amorphous carbon content of the sample. Similar situation is reported on the other studies in literature and oxidation of amorphous carbon below 400°C is mentioned.

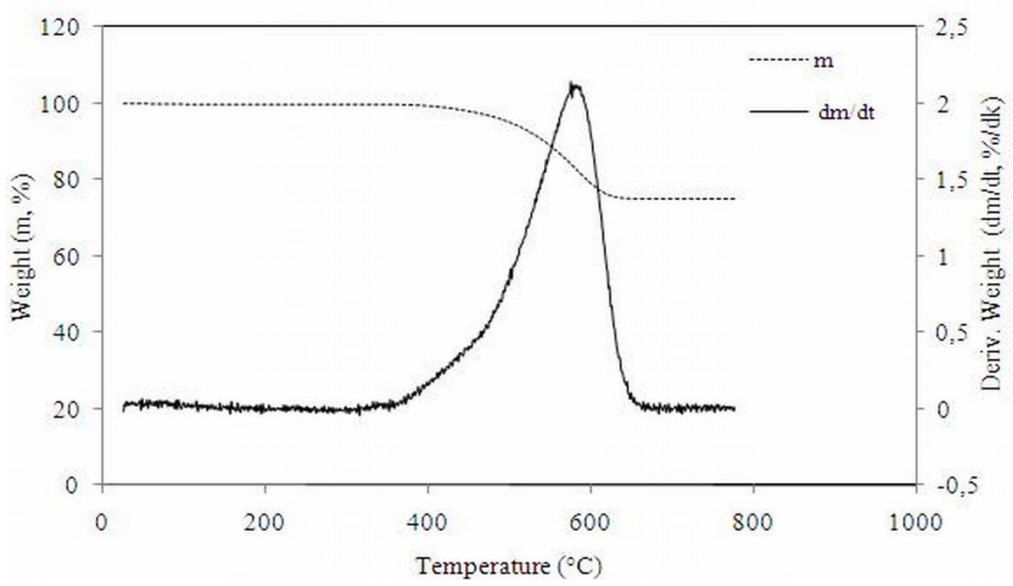

Figure 5.3: TG ve DTH curves of SWCNT synthesized at 800°C.

TG analysis of the purified SWCNTs by 3 M HNO3 for 3 h at 120 °C was performed in air atmosphere with a ramp of 5 °C/min between 25 and 800 °C. Purification yield was calculated according to the following equation (5.2):

$$\text{Purification yield (\%)} = (w_0 - w_t) / w_0 * 100 \qquad \textbf{(5.2)}$$

Purification yield (%) where w_0 is the metal content of as-grown SWCNT (%) and w_t is the metal content of purified SWCNT (%).The sample purified by HNO_3 demonstrated a residual weight of nearly 1.19% belonging to catalyst particles which suggested efficient removal of metallic catalyst (Figure 5.4) and 98.39% purity level.

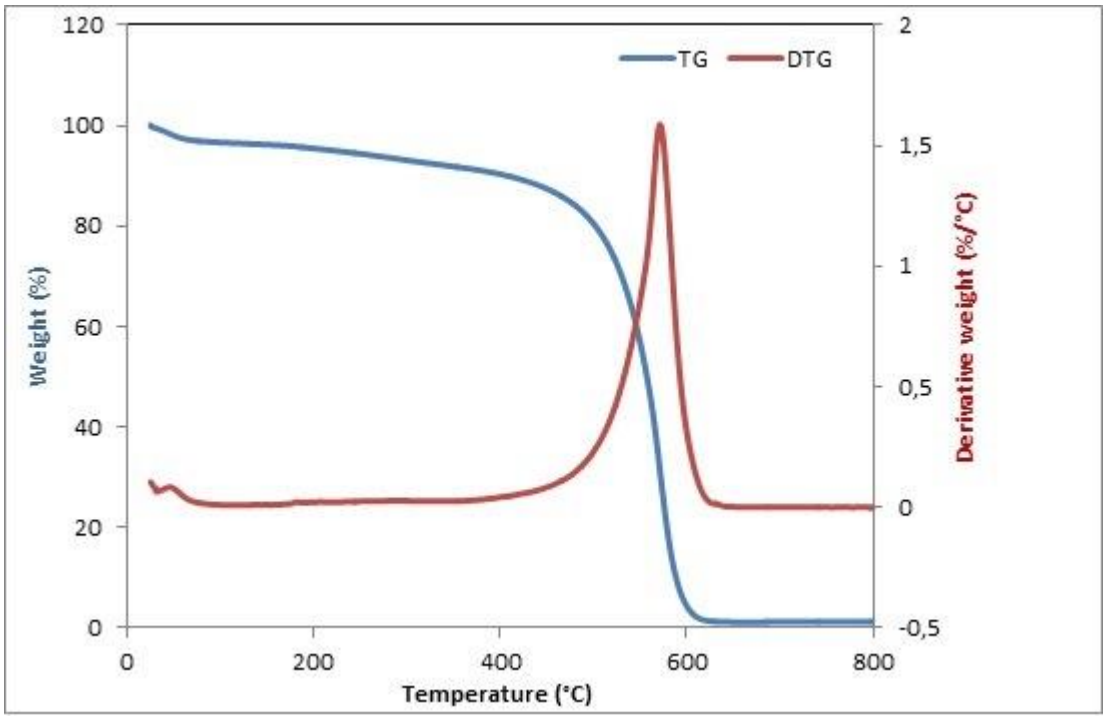

Figure 5.4: TG and DTG curves of SWCNTs purified by HNO_3.

5.2 Evalution of Thin Film Results

This part discusses the dispersion and deposition routes of SWCNT thin films. Two different types of dispersing agents were examined to achieve a homogeneous SWCNT solution. An ultrasonic homogenizer and an ultrasonic bath were used for dispersion and the results were compared. It has been found that ultrasonic homogenizer was more effective for SWCNT dispersions.

Vacuum filtration and spray coating techniques were utilized for the deposition of SWCNT thin films. Optoelectronic properties of the films were examined for different SWCNT densities. Moreover, SWCNT thin film functionalizations with acid and heat treatments were also investigated in order to improve the electrical conductivities of the thin films.

5.2.1 Evaluation of thin films prepared by vacuum filtration

5.2.1.1 Effect of sonication and centrifugation

Due to the agglomeration tendency of CNTs, sonication process is quite important parameter to obtain homogeneous SWCNT dispersion. Ultrasonic bath and homogenizer were utilized during this process. Ultrasonic homogenizer was utilized

for only 5 minutes and homogeneous SWCNT dispersion was obtained. However ultrasonic bath was utilized for 6 hours, the dispersion of SWCNTs was still poor. Figure 5.5 shows the SEM images of SWCNT thin films which their solutions prepared with two different sonication process. SWCNT dispersion prepared by ultrasonic bath is shown in Figure 5.5 (a). It can be clearly seen that there are still the large bundles of SWCNT. Figure 5.5 (b) shows a homogeneous dispersion of SWCNT prepared by an ultrasonic homogenizer. On the other hand, second sonication is quite effective for homogeneity.

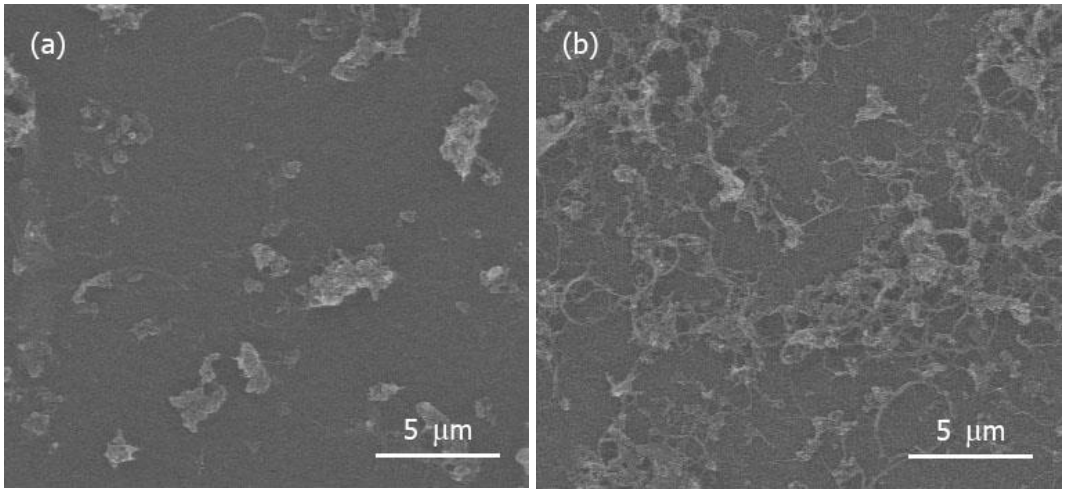

Figure 5.5: SEM images of the SWCNT thin films prepared different sonication processes a) ultrasonic bath b) ultrasonic homogenizer.

Experimental results revealed that an additional centrifuge step following the sonications was effective in enhancing the performance of SWCNT thin films. Removing large SWCNT bundles from the dispersion increase the transmittance of the SWCNT thin films.

5.2.1.2 Effect of density

Optoelectronic properties of thin film were affected SWCNT solution concentration and different filtration volumes. These parameters directly related to SWCNT thin films densities. The densities were calculated by the simple relation and found as $1.05x10^{-4}$, $2.12x10^{-4}$ and $3.19x10^{-4}$ mg/mm^2 for the filtration volumes of 2.5, 5 and 7.5 ml, respectively.

Figure 5.6 shows the SEM images of SWCNT thin films prepared with three filtration volumes of 2.5, 5 and 7.5 ml. It is seen from this Figure that SWCNT

connections are poor for the SWCNT thin film prepared with a filtration volume of 2.5 ml. In contrast, the connections of SWCNTs higher for the SWCNT thin film prepared with a filtration volume of 7.5 ml.

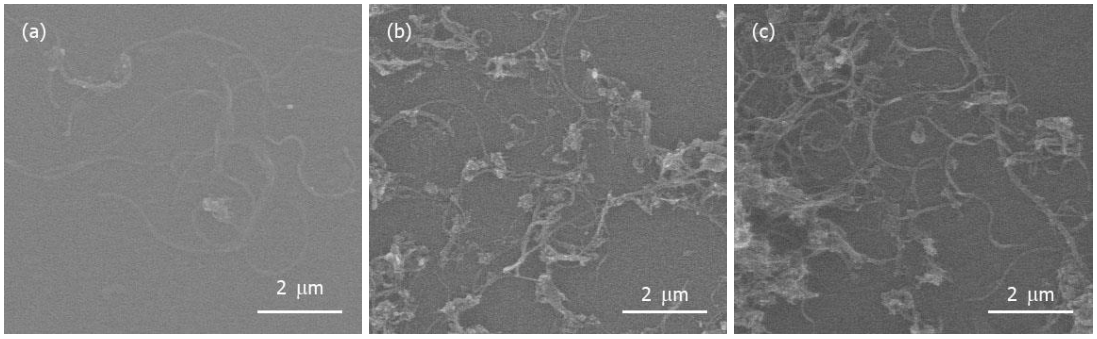

Figure 5.6: SEM images of the SWCNT thin films prepared from filtration volumes of (a) 2.5 ml, (b) 5 ml and (c) 7.5 ml.

Figure 5.7 shows the sheet resistance versus optical transmittance of the SWCNTs thin films. The plot proves increasing film density improves conductivity of films due to an increase in number of conducting pathways along the network. However, optical transmittance decreases with film density as excepted.

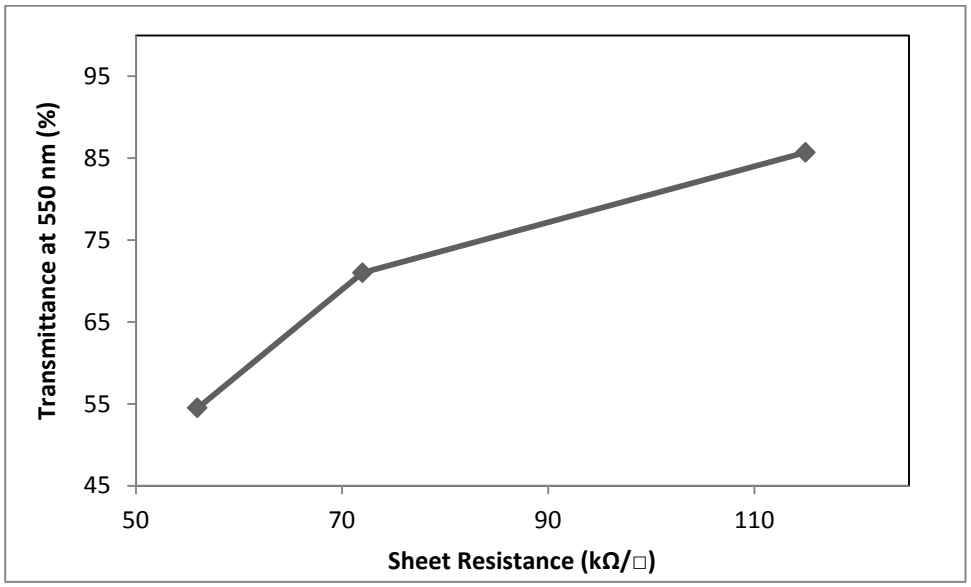

Figure 5.7: Sheet resistance vs. optical transmittance plot for the SWCNT thin films.

5.2.1.3 Effect of surfactant

SWCNT dispersions with two different surfactant types (SDS and Triton X-405) were prepared and compared. All solutions were sonicated using an ultrasonic homogenizer for 5 minutes and after centrifugation steps again sonicated for 5 minutes. It is seen from Figure 5.8 that the films from SDS dispersed SWNT

solutions were homogeneous whereas SWCNTs prepared with Triton X-405 solution were poor dispersed.

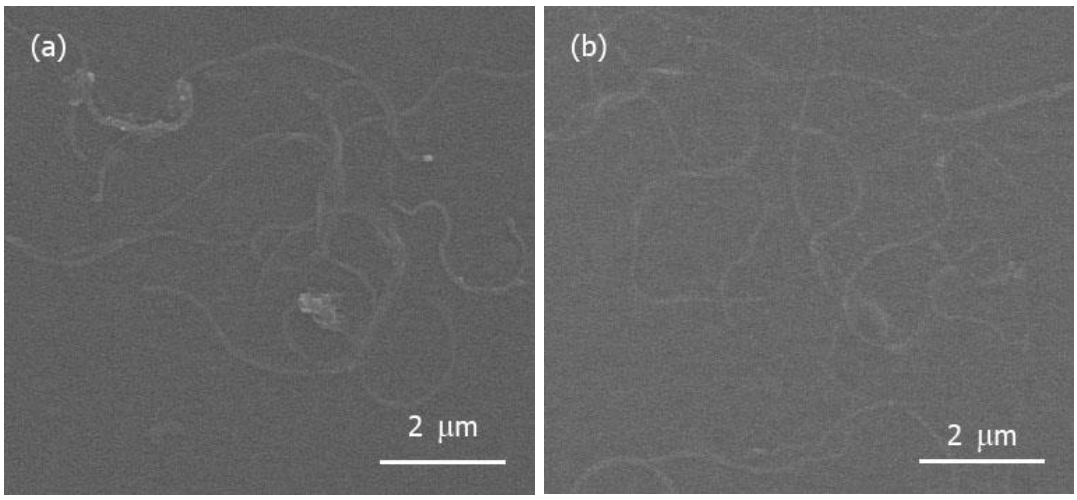

Figure 5.8: SEM images of the SWCNT thin films prepared with (a) Triton X-405 and (b) SDS.

Figure 5.9 exhibits the sheet resistance versus optical transmittance plot for SWNT thin films prepared from dispersions of SWNTs with different surfactants. It is found that the films fabricated from SDS dispersed SWNT solutions show the best optoelectronic performance. SDS provides the best dispersion due to the strong electrostatic attraction of its own molecules with the nanotube surfaces. As a result they have lower sheet resistance values under similar transmittance values

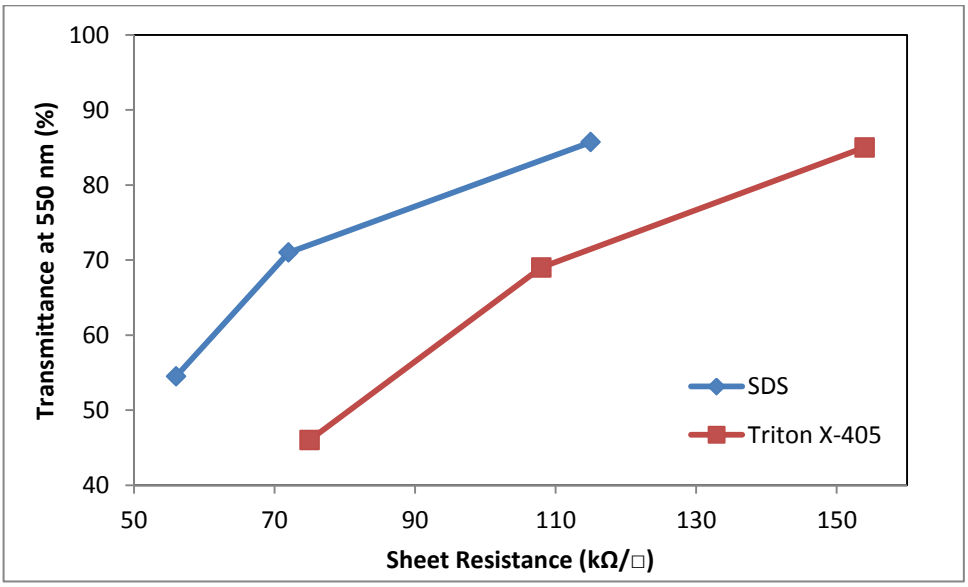

Figure 5.9: Sheet resistance vs. optical transmittance plot for the SWCNT thin films prepared with different surfactants.

5.2.1.4 Effect of acid treatments

In order to improve the conductivity, SWNT thin films were immersed in HNO_3 and $SOCl_2$ baths to improve the conductivity. It is found that sheet resistance of the SWNT thin films can be decreased by a factor of 3 after these treatments. Figure 5.10 and Figure 5.11 shows that sheet resistance decrease after treatment with $SOCl_2$ and HNO_3. The enhancement in electrical conductivity of the films depends on two factors. One of them is the removal of the insulating residual surfactant. Residual SDS on the SWNTs sidewalls cannot be washed away completely during the vacuum filtration process and limit the interaction between nanotubes. Nitric acid treatment was attributed to the removal of SDS, which is an insulating substance. The other factor is that $SOCl_2$ bath was increased charge carriers because of the p-type doping effect. Beside, after immersing the films into a $SOCl_2$ bath the carboxylic acid groups which created on the CNT surface due to HNO_3 treatment were substituted with acyl chloride groups. These groups contribute holes to the SWNTs and improve the overall conductivity of the films.

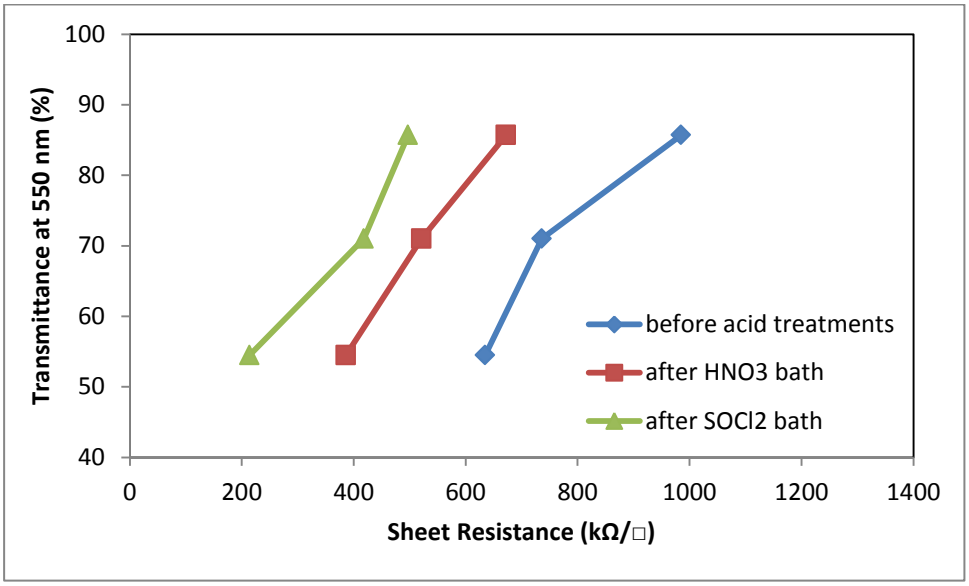

Figure 5.10: Sheet resistance vs. optical transmittance plot for acid functionalized thin films prepared with SDS.

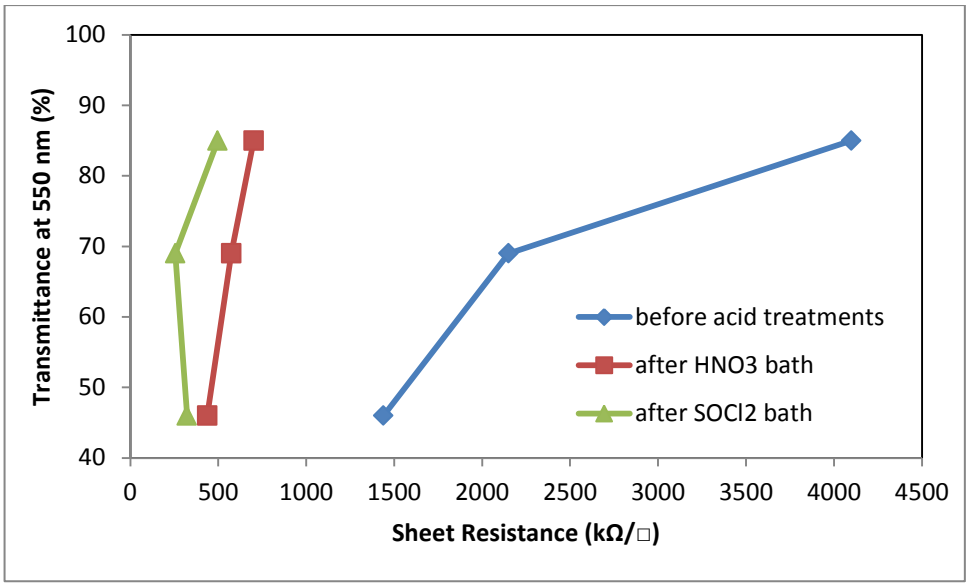

Figure 5.11: Sheet resistance vs. optical transmittance plot for acid functionalized SWCNT thin films prepared with Triton X-405.

5.2.1.5 Effect of heat treatments

In order to improve the conductivity, heat treatment was also applied to SWCNT thin films. During the vacuum filtration process, residual surfactant on the SWCNTs sidewalls cannot be washed away completely. Heat treatment has been effective to remove surfactants remaining in SWCNTs. Figure 5.12 and Figure 5.13 show that sheet resistance decrease 12 times after heat treatment for films prepared both SDS and triton X405 surfactants. Compared to acid treatment, heat treatment was found to be more effective to improve the conductivity of SWCNT thin films.

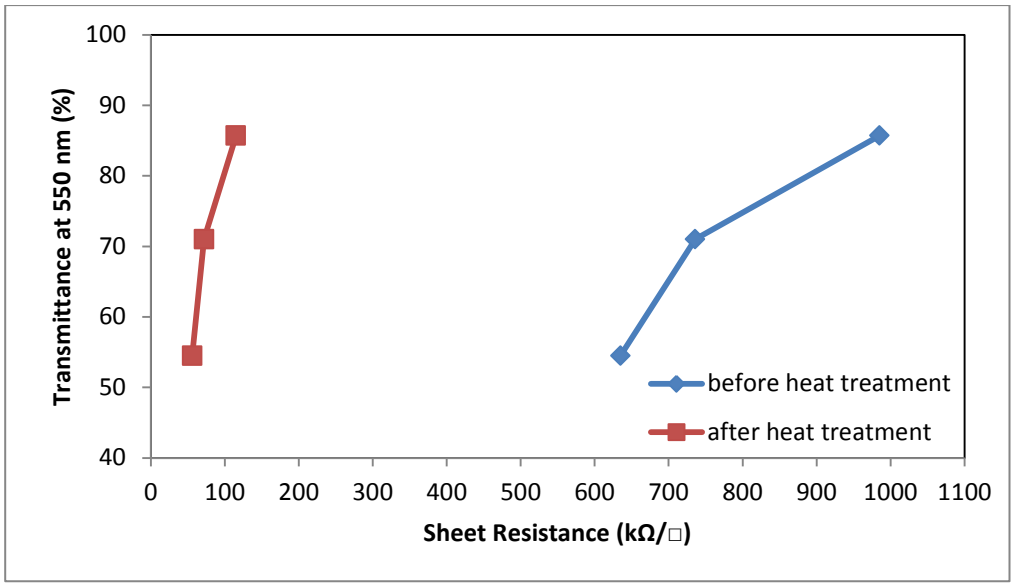

Figure 5.12: Sheet resistance vs. optical transmittance plot for post deposition annealing applied SWCNT thin films prepared with SDS.

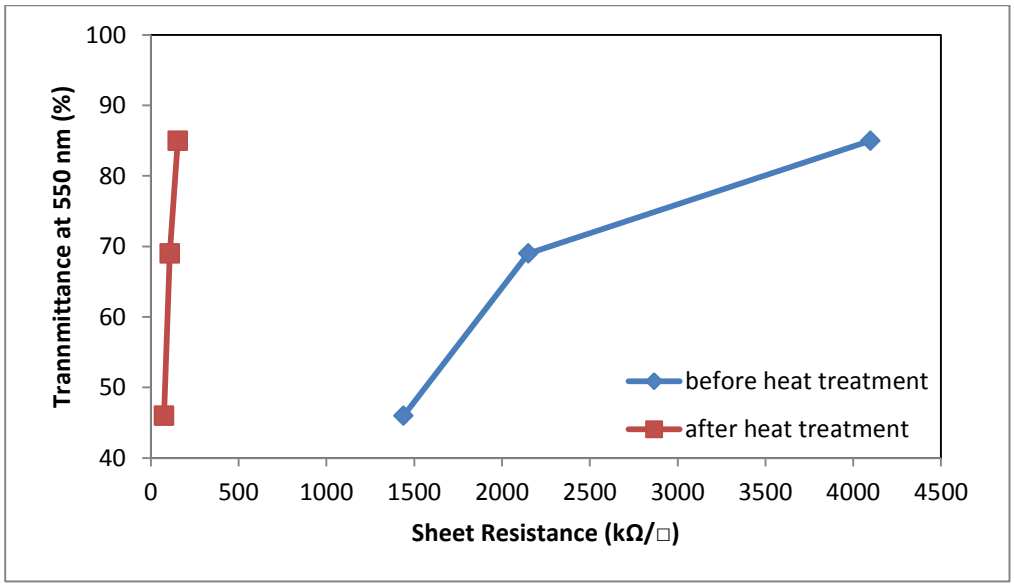

Figure 5.13: Sheet resistance vs. optical transmittance plot for post deposition annealing applied SWCNT thin films prepared with Triton X-405.

5.2.1.6 Effect of using AgNWs

In order to improve conductivity, AgNWs with 0.05 and 0.07 mg/ml concentrations were added to SWCNT solution. It is found that the sheet resistance of the SWCNT thin films dramaticaly decrease when AgNWs were added. Figure 5.14 shows that when the concentration of AgNWs within SWCNT solution increase, sheet resistances of SWCNT thin films decrease from 250 to 95 Ω/□ , whereas optical

transmittance decreases. Figure 5.15 and Figure 5.16 shows the SEM images of SWCNT thin films prepared with AgNWs at different addition concentration. It is seen the homogeneous dispersion of AgNW-SWCNT thin films prepared at two AgNWs concentrations.

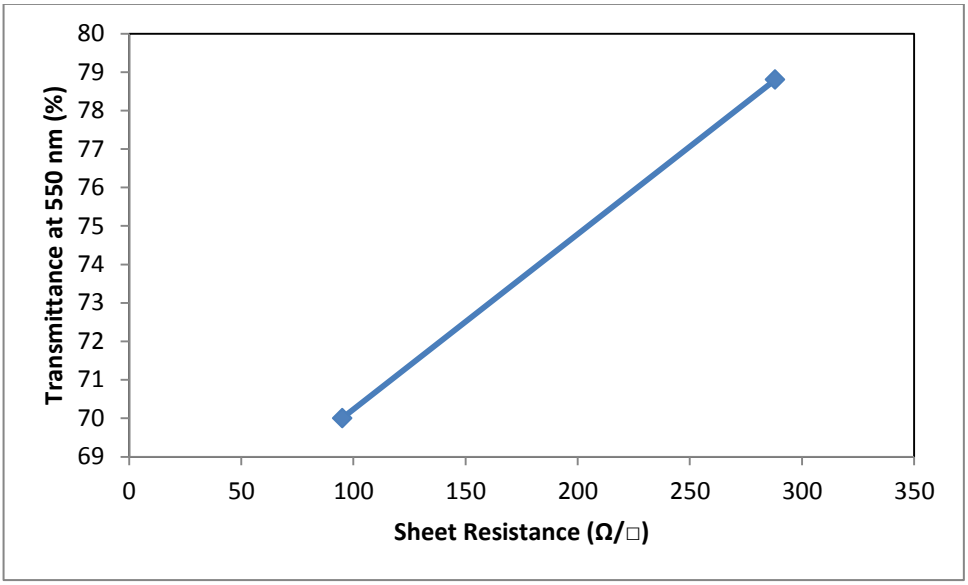

Figure 5.14: Sheet resistance vs. optical transmittance plot of the AgNW-SWCNT thin films prepared at two different AgNWs concentrations.

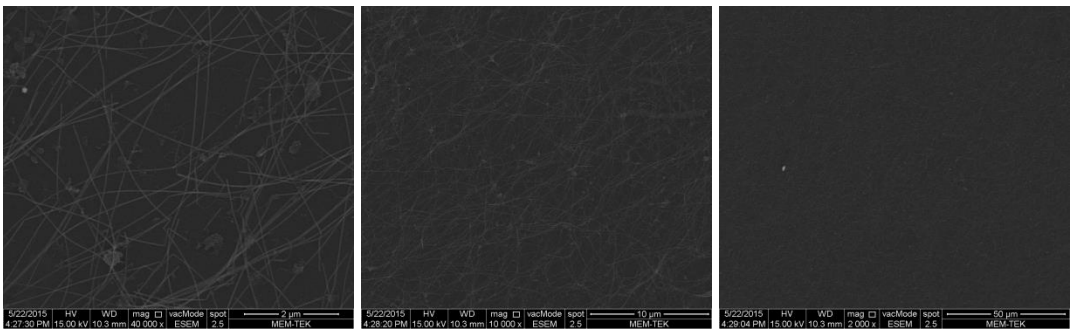

Figure 5.15: SEM images of the AgNW-SWCNT thin films prepared at the AgNWs concentration of 0.05 mg/ml.

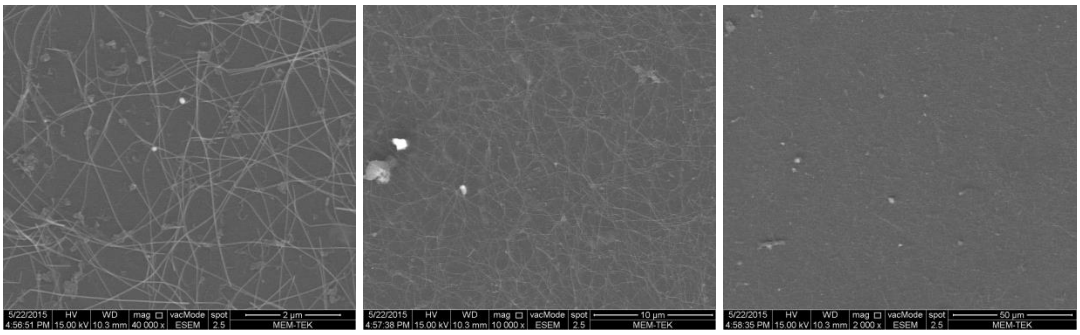

Figure 5.16: SEM images of the AgNW-SWCNT thin films prepared at the AgNWs concentration of 0.07 mg/ml.

5.2.2 Evaluation of thin films prepared by spray coating

Spray coating is a fast and easily scalable technique, nevertheless optoelectronic properties of the spray deposited SWCNT films did not show the well performance. In the study, SWCNT thin films were spray coated on 1.5 x 1.5 cm glass substrates using 10 ml solution with 1 mg/ml SWCNT concentration. SWCNT dispersions were performed with two different surfactant types and sheet resistance values for the spray deposited SWCNT thin films were compared. The sheet resistances of the films fabricated from SWCNT solutions dispersed with SDS and Triton X-405 were determined as 8 MΩ/sq and 11 MΩ/sq, respectively. To improve conductivity the films were immersed in HNO_3 bath followed by $SOCl_2$ immersion. Following these post deposition treatments, the sheet resistance of SWCNT thin films were decreased to 0.3 MΩ/sq and 0.4 MΩ/sq, respectively. In addition, heat treatment was also applied to SWCNT thin films due to decrease resistivity. After the heat treatment, the sheet resistance values are measured as 0.13 MΩ/sq and 0.20 MΩ/sq, respectively. Minimum sheet resistance value for the spray deposited SWCNT thin films was measured as 0.13 MΩ/sq. The uniformity of SWCNT films is crucial factor for the high conductivity. The spray coating parameters such as scan speed, nozzle frequency and substrate temperature should all be individually controlled to prevent droplet formation on the film surface. Therefore, the film uniformity could not to be easily maintained like in vacuum filtration process.

Removal of the surfactants from spray coated SWCNT thin films was also a problem. Following spray coating, SWCNT thin films were only dipped into distilled water to remove the residual surfactant. Figure 5.17 shows that SEM images of SWCNT thin films deposited by spray coating from SWCNT solution dispersed with SDS and Triton X-405. It is clearly seen that distilled water did not remove the residual surfactants effectively.

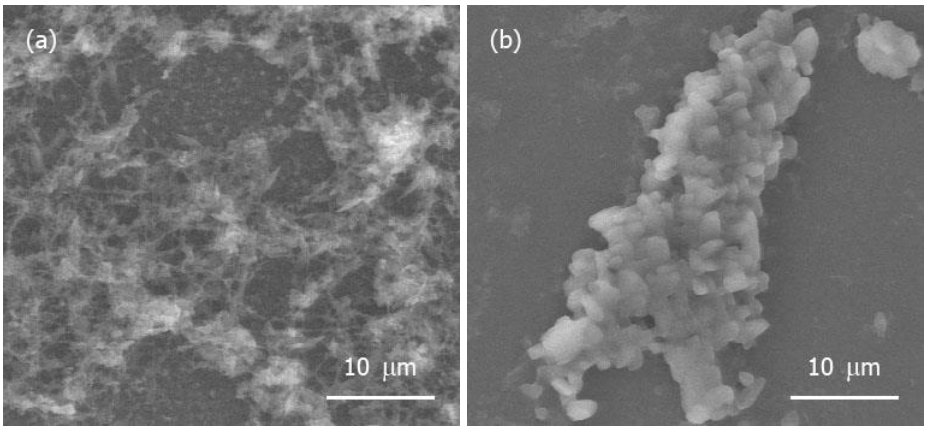

Figure 5.17: SEM images of SWCNT thin films deposited by spray coating from dispersed SWCNT solution with (a) SDS and (b) Triton X-405.

6. CONCLUSIONS AND RECOMMENDATIONS

In this study, SWCNT thin films fabricated via vacuum filtration and spray coating methods. The effects of surfactants, sonication types, density of SWCNTs, acid and heat treatments were investigated on the thin film fabrication and its performance. Important findings of this study are as follows:

6.1 Concluding Remarks

1. SWCNTs were synthesized by chemical vapor deposition of acetylene on Fe/MgO catalyst at 800°C and purified by 3M HNO_3 at 98.39 % purity level.
2. SWCNT thin films were fabricated by spray coating and vacuum filtration methods for different parameters (surfactant and sonication types, density of SWCNT, acid and heat treatments etc.).
3. Effect of surfactant is one of the important parameters to prepare homogeneous SWCNT solutions. SDS assisted SWCNT dispersion was the most homogeneous solution when compared Triton X-405.
4. Sonication type is the other crucial factor for well dispersed SWCNTs in distilled water. Homogeneous and stable solutions were obtained only after five minutes by ultrasonic homogenizer. Bath sonication was revealed poor dispersion even after 6 hours of sonication.
5. Centrifugation step provides separating large SWCNT bundles. Thus, optical transparency of thin films was decrease and conductivity of thin films was increased. Second sonication step were assisted again the dispersibility of new solution which separated bundles.
6. Density of SWCNT on the glass substrate was directly affected sheet resistance and optical transmittance of SWCNT thin films. Increasing density was decreased transmissivity nevertheless contributed conductivity.
7. When compared the coating methods, thin films fabricated by vacuum filtration has better properties than spray coating. Although spray coating

method was attempted for large area applications, homogeneous thin films were not obtained.

8. Optoelectronic measurements of the fabricated SWCNT thin films revealed that post deposition acid treatments were enhanced conductivity of SWCNT thin films.
9. Annealing is the considerable efficient treatment to fabricate SWCNT thin films. There was tremendous decrease (approximately 12 times) in sheet resistance of SWCNT thin films with heat treatment due to get rid of the surfactants successfully.
10. AgNWs/SWCNT thin films were revealed the best optoelectronic performances. When the concentration of AgNWs within SWCNT solution increase, sheet resistances of SWCNT thin films decrease from 250 to 95 Ω/□**,** whereas optical transmittance decreases.

6.2 Recommendations

The results of this dissertation provide further optimism for the potential of SWCNT transparent electrodes as an alternate for ITO in organic electronics. Due to the one dimensional nature of SWCNTs, an extraordinary approach will be required to increase their utility in electronic devices. Overall, the unique optoelectronic properties of single wall carbon nanotubes, which have the mechanical stability exhibited in thin nanotube networks, make SWCNT transparent electrodes a promising candidate for organic photovoltaic and touch screen display integration.

Although spray coating is a fast, easily scalable technique and attempted for large area applications, homogeneous thin films were not obtained. In the further studies, different SWCNT dispersion concentrations can be examined to obtain the best optoelectronic properties.

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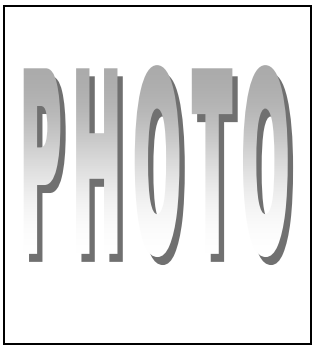
CURRICULUM VITAE



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